

Process for the Preparation of Silicon-Containing Composite Particles

This invention relates to processes for the production of silicon-containing composite particles that are suitable for use as anode active materials in rechargeable lithium-ion batteries.

A typical lithium-ion battery (LIB) comprises an anode, a cathode and a lithium-containing electrolyte. The anode generally comprises a metal current collector provided with a layer of an electroactive material, defined herein as a material which is capable of inserting and releasing lithium ions during the charging and discharging of a battery. The terms "cathode" and "anode" are used herein in the sense that the battery is placed across a load, such that the anode is the negative electrode. When a LIB is charged, lithium ions are transported from the cathode via the electrolyte to the anode and are inserted into the electroactive material of the anode as intercalated lithium atoms. The term "battery" is used herein to refer both to devices containing a single lithium-ion cell and to devices containing multiple connected lithium-ion cells.

LIBs were developed in the 1980s and 1990s and have since found wide application in portable electronic devices. The development of electric or hybrid vehicles in recent has created a significant new market for LIBs and renewable energy sources have created further demand for on-grid energy storage which can be met at least in part by LIB farms. Overall, global production of LIBs is projected to grow from around 290 GWh in 2018 to over 2,000 GWh in 2028.

Alongside the growth in total storage capacity, there is significant interest in improving the gravimetric and/or volumetric capacities of rechargeable metal-ion batteries such that the same energy storage is achieved with less battery mass and/or less battery volume. Conventional LIBs use graphite as the anode electroactive material. Graphite anodes can accommodate a maximum of one lithium atom for every six carbon atoms resulting in a maximum theoretical specific capacity of 372 mAh/g in a lithium-ion battery, with a practical capacity that is somewhat lower (ca. 340 to 360 mAh/g).

Silicon is a promising alternative to graphite because of its very high capacity for lithium (see, for example, Insertion Electrode Materials for Rechargeable Lithium Batteries, Winter, M. *et al.* in Adv. Mater. 1998, 10, No. 10). Silicon has a theoretical maximum specific capacity of about 3,600 mAh/g in a lithium-ion battery (based on $\text{Li}_{15}\text{Si}_4$). However, the

- intercalation of lithium into bulk silicon results in expansion of the silicon material by up to 400% of its original volume which can lead to failure of the battery. Repeated charge-discharge cycles cause significant mechanical stress, resulting in fracturing and delamination of the silicon. The formation of a solid electrolyte interphase (SEI) layer on the silicon surface consumes the electrolyte and newly exposed silicon surfaces on fracture surfaces results in further electrolyte decomposition and increased thickness of the SEI layer and irreversible consumption of lithium. These failure mechanisms collectively result in an unacceptable loss of electrochemical capacity over successive charging and discharging cycles.
- 10 The applicant has previously reported the development of a class of electroactive materials having a composite structure in which electroactive materials, such as silicon, are deposited into the pore network of a highly porous conductive particulate material, e.g. a porous carbon material (see WO 2020/095067 and WO 2020/128495). The silicon in these materials is finely divided with individual silicon structures having dimensions of the order
- 15 of a few nanometres or less which therefore undergo minimal stress and strain during charging and discharging. As the silicon is confined to the pore volume of a porous material, exposure of the silicon surfaces to electrolyte is minimised, effectively limiting the extent of SEI formation. As a result, these materials exhibit good reversible capacity retention over multiple charge-discharge cycles.
- 20 The materials described in WO 2020/095067 and WO 2020/128495 have been synthesized by chemical vapour infiltration (CVI) in different reactor systems (static, rotary and FBR). The porous conductive particles are contacted with a silicon precursor, typically silane gas, at atmospheric pressure and at temperatures between 400 to 700 °C. Reaction rates at these temperatures are fast, however, the silicon precursor molecules need to go through
- 25 a tortuous path to access pore spaces of only a few nanometres in diameter. This means, that to obtain a homogeneous infiltration in such reactor systems, the reaction temperature needs to be relatively high to avoid mass transfer becoming a rate limiting step. Furthermore, the silicon precursor generally needs to be used at high dilution in an inert gas. Too high a concentration of the silicon precursor can result in rapid and uncontrolled
- 30 deposition of silicon deposition in the outermost pores which then blocks access to much of the available pore volume. As a result, the deposited silicon does not have the fine structure associated with deposition in narrow pores, but is coarse and exposed and therefore demonstrates poor cycling behaviour. However, the use of low concentrations of the silicon

precursor means that the reaction time to achieve the necessary silicon loading in the composite particles is relatively long, reducing throughput.

Systems that are operated by batch dosing of silicon precursor have further disadvantages. In order to obtain composite particles with the required content of silicon, several cycles of CVI deposition are necessary. At the beginning of each cycle, a charge of silicon precursor is introduced into the reactor. The reactor temperature generally decreases as silicon precursor is added, necessitating heating of the reactor to return the feedstock to reaction temperature. Removal of by-product gases after each cycle is also required. Consequently, the overall manufacturing time of the composite particles is long and the throughput of such systems is poor.

These systems are therefore ill-suited to scale-up and producing large quantities of material is difficult.

There is therefore a need in the art for improved processes for preparing silicon-containing composite particles that are suitable for use as electroactive materials in LIBs. In particular, there is a need for processes for preparing such composite particles on a large-scale, with high throughput, while maintaining product quality.

In a first aspect, the invention provides a process for preparing composite particles, the process comprising the steps of:

- (a) providing a charge of porous particles in a pressure reactor, wherein the charge of porous particles has a total surface area of at least $8 \times 10^4 \text{ m}^2$ per litre of reactor volume ($\text{m}^2/\text{L}_{\text{RV}}$);
- (b) continuously supplying a silicon precursor gas to the pressure reactor while subjecting the porous particles to reaction conditions effective to cause deposition of silicon in the pores of the porous particles, thereby providing composite particles comprising a porous particle framework and silicon within the pores of the porous particle framework, wherein the reaction conditions include agitation of the particles.

The invention therefore relates in general terms to a process for preparing a composite particulate material in which silicon deposited into the pore network of porous particles by a process of chemical vapour infiltration, i.e. via the thermal decomposition of a silicon-containing precursor compound. The composite particles therefore comprise a first component in the form of the porous particles, these forming a framework that supports a

second component in the form of a plurality of silicon domains that are disposed within the pore structure of the porous particle framework. As used herein, the term "silicon domain" refers to a body of silicon having maximum dimensions that are determined by the location of the silicon within the pore structure of the porous particles.

- 5 The process of the invention is operated as continuous with respect to the gaseous silicon precursor and batch with respect to the porous particles. This mode of operation is referred to herein as a semi-continuous reaction. The term semi-continuous is used to distinguish from a non-continuous or "batch-type" reaction mode and a fully continuous reaction mode.

10 In a batch-type reaction mode, a batch of the starting material (porous particles) is added to the reactor along with a charge of the silicon precursor. The reaction is then sealed and the CVI reaction is initiated and allowed to progress for a specified period. The CVI reaction is then stopped and the reactor may be charged again with a further charge of the silicon precursor. A batch of product (composite particles) is withdrawn from the reactor once the target amount of silicon has been deposited.

- 15 In a fully continuous reaction mode, both the porous particles and the silicon precursor are supplied continuously to the reactor and a composite particle product is withdrawn continuously from the reactor. Accordingly, the supply of both reagents (porous particles and silicon precursor) occurs simultaneously with the reaction in progress.

20 In a semi-continuous reaction mode, a batch of the porous particles is added to the reactor but the gaseous silicon precursor is added to the reactor as a continuous feed simultaneously with the reaction in progress. Preferably, the withdrawal of an effluent gas also occurs simultaneously with the reaction in progress.

25 In principle, semi-continuous operation does not exclude the possibility of deviations in the rate of flow of the silicon precursor gas or the effluent gas. For instance, a continuous reactor may operate in a pulsed mode. For example, the flow rate of the silicon precursor gas into the pressure reactor may be reduced to aid the withdrawal of effluent gas from the pressure reactor. Alternatively, the silicon precursor gas may be introduced into the pressure reactor at a constant pressure.

30 Operating the pressure reactor in a semi-continuous mode means that the CVI deposition proceeds under conditions where fresh silicon precursor gas is added before byproducts are removed fully from the system. Accordingly, diffusion of the silicon precursor gas to the

surfaces of the porous particles occurs simultaneously with diffusion of byproduct gases from the surfaces of the porous particles. This presents a substantially more complex system from the perspective of reactor control. Particularly in the case of porous particles comprising fine pore structures, the silicon precursor gas must diffuse through the pore structure of the porous particles prior to deposition. If the diffusion rate is too slow, then silicon may be deposited on the external surfaces of the porous particles, such that the composite particles contain large, coarse silicon structures which are unsuitable for use in lithium ion batteries.

The present invention addresses this problem by providing a reaction in design in which the diffusion pathways between the bulk volume of the pressure reactor and the surfaces of the composite particles are controlled by a defined ratio of porous particle surface area to reactor volume.

As the silicon precursor gas is continuously added to the reactor it mixes with byproducts, resulting in a consistent concentration of silicon precursor. Compared to systems that are operated by batch dosing of silicon precursor gas, the porous particles are contacted by a more consistent concentration of silicon precursor throughout the deposition.

As the CVI deposition takes place in a consistent but relatively dilute phase, it is expected to occur at a slower rate compared to systems that are operated by batch dosing of silicon precursor gas, but the degree of control over the deposition reaction is enhanced as gradients of pressure and temperature in the pressure reactor are eliminated, such that the porous particles are exposed to more consistent conditions, including temperature, pressure and concentration of silicon precursor. Increased control of the reaction conditions results in better control of important properties of the composite particles, including silicon content, surface area and amount of coarse silicon.

Furthermore, the process results in increased throughput overall by reducing production downtime associated with fluctuations in pressure and temperature that are inherent in systems that are operated by batch dosing of silicon precursor gas, since these generally require multiple repeat dosings of the charge of silicon precursor gas to achieve the required silicon content in the composite particles.

The present invention relates in particular to a reaction regime in which the charge of porous particles in the reactor is controlled to provide a specified total surface area per unit volume of the reactor. Since the deposition of silicon occurs at the surfaces of the porous particles,

optimum reaction efficiency is obtained when the total surface area available for deposition of silicon is tailored to the reactor volume. If the surface area of the porous particles is too low relative to the reactor volume then the deposition reaction is mass transfer limited, meaning that diffusion of the silicon precursor to the porous particle surface becomes a rate-limiting factor. As a consequence, the residence time of the silicon precursor gas in the reactor is increased resulting in poor throughput and low volumetric reactor efficiency.

The total surface area of the charge of porous particles refers to the BET surface area multiplied by the mass of the charge of porous particles. The term "BET surface area" as used herein should be taken to refer to the surface area per unit mass calculated from a measurement of the physical adsorption of gas molecules on a solid surface, using the Brunauer–Emmett–Teller theory, in accordance with ISO 9277:2022.

The charge of porous particles in step (a) preferably has a total surface surface area of at least $9 \times 10^4 \text{ m}^2/\text{L}_{\text{RV}}$, more preferably at least $1.0 \times 10^5 \text{ m}^2/\text{L}_{\text{RV}}$, more preferably at least $1.1 \times 10^5 \text{ m}^2/\text{L}_{\text{RV}}$, more preferably at least $1.2 \times 10^5 \text{ m}^2/\text{L}_{\text{RV}}$, more preferably at least $1.3 \times 10^5 \text{ m}^2/\text{L}_{\text{RV}}$, more preferably at least $1.4 \times 10^5 \text{ m}^2/\text{L}_{\text{RV}}$, more preferably at least $1.5 \times 10^5 \text{ m}^2/\text{L}_{\text{RV}}$, more preferably at least $1.6 \times 10^5 \text{ m}^2/\text{L}_{\text{RV}}$, more preferably at least $1.8 \times 10^5 \text{ m}^2/\text{L}_{\text{RV}}$, more preferably at least $2.0 \times 10^5 \text{ m}^2/\text{L}_{\text{RV}}$, more preferably at least $2.2 \times 10^5 \text{ m}^2/\text{L}_{\text{RV}}$, more preferably at least $2.5 \times 10^5 \text{ m}^2/\text{L}_{\text{RV}}$.

The total surface area of the charge of porous particles in step (a) is preferably no more than $1.0 \times 10^6 \text{ m}^2/\text{L}_{\text{RV}}$, more preferably no more than $9.0 \times 10^5 \text{ m}^2/\text{L}_{\text{RV}}$, more preferably no more than $8.0 \times 10^5 \text{ m}^2/\text{L}_{\text{RV}}$, more preferably no more than $7.0 \times 10^5 \text{ m}^2/\text{L}_{\text{RV}}$, more preferably no more than $6.0 \times 10^5 \text{ m}^2/\text{L}_{\text{RV}}$, more preferably no more than $5.0 \times 10^5 \text{ m}^2/\text{L}_{\text{RV}}$, more preferably no more than $4.0 \times 10^5 \text{ m}^2/\text{L}_{\text{RV}}$. The maximum total surface area of the charge of porous particles is limited not only by the volumetric capacity of the reactor, but also by the need to obtain a homogenous product. If the surface area of the porous particles is too high, it is difficult to achieve homogenous distribution of the silicon precursor throughout the mass of porous particles prior to reaction, resulting in impaired product homogeneity.

Accordingly, the total surface area of the charge of porous particles in step (a) is preferably in the range from 8.0×10^4 to $1.0 \times 10^6 \text{ m}^2/\text{L}_{\text{RV}}$, more preferably from 1.0×10^5 to $8.0 \times 10^5 \text{ m}^2/\text{L}_{\text{RV}}$, more preferably from 1.5×10^5 to $6.0 \times 10^5 \text{ m}^2/\text{L}_{\text{RV}}$, more preferably from 2.0×10^5 to $5.0 \times 10^5 \text{ m}^2/\text{L}_{\text{RV}}$.

The porous particles preferably comprise a three-dimensionally interconnected open pore network comprising micropores and/or mesopores and optionally a minor volume of macropores. In accordance with conventional IUPAC terminology, the term “micropore” is used herein to refer to pores of less than 2 nm in diameter, the term “mesopore” is used
5 herein to refer to pores of 2-50 nm in diameter, and the term “macropore” is used to refer to pores of greater than 50 nm diameter.

References herein to the volume of micropores, mesopores and macropores in the porous particles, and also any references to the distribution of pore volume within the porous particles, relate to the internal pore volume of the porous particles used as the starting
10 material in step (a) of the claimed process, i.e. prior to deposition of silicon into the pore volume in step (c).

Preferably, the total volume of micropores and mesopores in the porous particles (i.e. the total pore volume in the range from 0 to 50 nm) is in the range from 0.4 to 2.2 cm³/g. Typically, the porous particles include both micropores and mesopores. However, it is not
15 excluded that porous particles may be used which include micropores and no mesopores, or mesopores and no micropores.

More preferably, the total volume of micropores and mesopores in the porous particles is at least 0.45 cm³/g, or at least 0.5 cm³/g, at least 0.55 cm³/g, or at least 0.6 cm³/g, or at least 0.65 cm³/g, or at least 0.7 cm³/g, or at least 0.75 cm³/g, or at least 0.8 cm³/g, at least
20 0.85 cm³/g, or at least 0.9 cm³/g, or at least 0.95 cm³/g, or at least 1 cm³/g. The use of high porosity conductive particles may be advantageous since it allows a larger amount of silicon to be accommodated within the pore structure.

The internal pore volume of the porous particles is suitably capped at a value at which increasing fragility of the porous particles outweighs the advantage of increased pore
25 volume accommodating a larger amount of silicon. Preferably, the total volume of micropores and mesopores in the porous particles is no more than 2 cm³/g, or no more than 1.8 cm³/g, or no more than 1.6 cm³/g, or no more than 1.5 cm³/g, or no more than 1.45 cm³/g, or no more than 1.4 cm³/g, or no more than 1.35 cm³/g, or no more than 1.3 cm³/g, or no more than 1.25 cm³/g, or no more than 1.2 cm³/g, or no more than 1.1
30 cm³/g, or no more than 1 cm³/g, or no more than 0.95 cm³/g, or no more than 0.9 cm³/g, or no more than 0.85 cm³/g, or no more than 0.8 cm³/g.

In some examples, the total volume of micropores and mesopores in the porous particles may be in the range from 0.45 to 2.2 cm³/g, or from 0.5 to 2 cm³/g, or from 0.55 to 2 cm³/g, or from 0.6 to 1.8 cm³/g, or from 0.65 to 1.8 cm³/g, or from 0.7 to 1.6 cm³/g, or from 0.75 to 1.6 cm³/g, or from 0.8 to 1.5 cm³/g.

- 5 In other examples, the total volume of micropores and mesopores in the porous particles may be in the range from 0.4 to 0.75 cm³/g, or from 0.4 to 0.7 cm³/g, or from 0.4 to 0.65 cm³/g, 0.45 to 0.75 cm³/g, or from 0.45 to 0.7 cm³/g, or from 0.45 to 0.65 cm³/g, or from 0.45 to 0.6 cm³/g.

- 10 In other examples, the total volume of micropores and mesopores in the porous particles may be in the range from 0.6 to 2 cm³/g, or from 0.6 to 1.8 cm³/g, or from 0.7 to 1.8 cm³/g, or from 0.7 to 1.6 cm³/g, or from 0.8 to 1.6 cm³/g, or from 0.8 to 1.5 cm³/g, or from 0.8 to 1.4 cm³/g, or from 0.9 to 1.5 cm³/g, or from 0.9 to 1.4 cm³/g, or from 1 to 1.4 cm³/g.

- 15 In preferred examples, the total volume of micropores and mesopores in the porous particles may be in the range from 0.55 to 1.4 cm³/g, or from 0.6 to 1.4 cm³/g, or from 0.6 to 1.3 cm³/g, or from 0.65 to 1.3 cm³/g, or from 0.65 to 1.2 cm³/g, or from 0.7 to 1.2 cm³/g, or from 0.7 to 1.1 cm³/g, or from 0.7 to 1 cm³/g, or from 0.75 to 0.95 cm³/g.

- 20 The PD₅₀ pore diameter of the porous particles may be no more than 30 nm, and optionally no more than 25 nm, or no more than 20 nm, or no more than 15 nm, or no more than 12 nm, or no more than 10 nm, or no more than 8 nm, or no more than 6 nm, or no more than 5 nm, or no more than 4 nm, or no more than 3 nm, or no more than 2.5 nm, or no more than 2 nm, or no more than 1.5 nm. The term "PD₅₀ pore diameter" as used herein refers to the volume-based median pore diameter, based on the total volume of micropores and mesopores (i.e. the pore diameter below which 50% of the total micropore and mesopore volume is found). Therefore, in accordance with the invention, at least 50% of
- 25 the total volume of micropores and mesopores is preferably in the form of pores having a diameter of less than 30 nm. Preferably, the PD₅₀ pore diameter is no more than 5 nm, more preferably no more than 4 nm, more preferably no more than 3 nm, more preferably no more than 2.5 nm, more preferably no more than 2 nm, more preferably no more than 1.5 nm.

- 30 For the avoidance of doubt, any macropore volume (pore diameter greater than 50 nm) is not taken into account for the purpose of determining PD₅₀ values.

The volumetric ratio of micropores to mesopores in the porous particles may range in principle from 100:0 to 0:100.

The process of the invention is particularly applicable to porous particles comprising a relatively high micropore volume. In particles with high microporosity, the process design
5 must balance the rate of reaction with the rate of diffusion of the silicon precursor gas into the micropores of the porous particles. If the reaction rate is too high relative to the diffusion rate, the silicon precursor gas reacts before it can diffuse into micropores, resulting in a material containing coarse silicon structures that are primarily in larger pores and on the particle surfaces. However, if the reaction rate is too low relative to the diffusion rate,
10 reaction throughput is poor. Since the reaction takes place in a continuous mode with respect to the silicon precursor gas, diffusion of the silicon precursor gas into the pores of the porous particles, and diffusion of byproduct gases out of the pores of the porous particles, is a factor which must be taken into account throughout the reaction. By controlling the relationship between the micropore volume and the total reactor volume
15 throughout which the silicon precursor gas can diffuse, the invention provides for improved control over diffusion effects in the reactor.

The micropore volume fraction is preferably at least 0.4, or at least 0.45, or at least 0.5, or at least 0.55, or at least 0.6, based on the total volume of micropores and mesopores in the porous particles.

20 The micropore volume fraction is preferably no more than 0.85, or no more than 0.8 based on the total volume of micropores and mesopores in the porous particles.

For example, the micropore volume fraction may be in the range from 0.4 to 0.85, or in the range from 0.45 to 0.85, or in the range from 0.5 to 0.8, or in the range from 0.55 to 0.8, or in the range from 0.6 to 0.8, based on the total volume of micropores and mesopores in the
25 porous particles. Alternatively, the micropore volume fraction may be greater than 0.8, or greater than 0.85, or greater than 0.9, or greater than 0.95, or greater than 0.98, based on the total volume of micropores and mesopores in the porous particles.

The pore size distribution of the porous particles may be monomodal, bimodal or multimodal. As used herein, the term "pore size distribution" relates to the distribution of
30 pore size relative to the cumulative total internal pore volume of the porous particles. A bimodal or multimodal pore size distribution may be preferred since close proximity between

micropores and pores of larger diameter provides the advantage of efficient ionic transport through the porous network to the silicon.

- The total volume of micropores and mesopores and the pore size distribution of micropores and mesopores are determined using nitrogen gas adsorption at 77 K down to a relative pressure p/p_0 of 0.8×10^{-6} using quenched solid density functional theory (QSDFT) in accordance with standard methodology as set out in ISO 15901-2:2022. Nitrogen gas adsorption is a technique that characterises the porosity and pore diameter distributions of a material by allowing a gas to condense in the pores of a solid. As pressure increases, the gas condenses first in the pores of smallest diameter and the pressure is increased until a saturation point is reached at which all of the pores are filled with liquid. The nitrogen gas pressure is then reduced incrementally, to allow the liquid to evaporate from the system. Analysis of the adsorption and desorption isotherms, and the hysteresis between them, allows the pore volume and pore size distribution to be determined. Suitable instruments for the measurement of pore volume and pore size distributions by nitrogen gas adsorption include the TriStar II and TriStar II Plus porosity analyzers, which are available from Micromeritics Instrument Corporation, USA, and the Autosorb IQ porosity analyzers, which are available from Quantachrome Instruments.

The charge of porous particles preferably has a total micropore volume of 10 to 400 cm³ per litre of reactor volume (cm³/L_{RV}), or 10 to 300 cm³/L_{RV}, or 10 to 200 cm³/L_{RV}.

- Preferably the charge of porous particles in step (a) has a total micropore volume of at least 15 cm³/L_{RV}, more preferably at least 20 cm³/L_{RV}, more preferably at least 25 cm³/L_{RV}, more preferably at least 30 cm³/L_{RV}, more preferably at least 35 cm³/L_{RV}, more preferably at least 40 cm³/L_{RV}, more preferably at least 45 cm³/L_{RV}, more preferably at least 50 cm³/L_{RV}, more preferably at least 55 cm³/L_{RV}, more preferably at least 60 cm³/L_{RV}, more preferably at least 65 cm³/L_{RV}, more preferably at least 70 cm³/L_{RV}.

- The total micropore volume of the charge of porous particles in step (a) is preferably no more than 350 cm³/L_{RV}, more preferably no more than 300 cm³/L_{RV}, more preferably no more than 250 cm³/L_{RV}, more preferably no more than 200 cm³/L_{RV}, more preferably no more than 180 cm³/L_{RV}, more preferably no more than 160 cm³/L_{RV}, more preferably no more than 140 cm³/L_{RV}, more preferably no more than 120 cm³/L_{RV}, more preferably no more than 110 cm³/L_{RV}, more preferably no more than 100 cm³/L_{RV}, more preferably no more than 90 cm³/L_{RV}, more preferably no more than 80 cm³/L_{RV}.

Accordingly, the micropore volume of the charge of porous particles in step (a) is preferably in the range from 15 to 350 cm³/L_{RV}, more preferably in the range from 20 to 300 cm³/L_{RV}, more preferably in the range from 25 to 250 cm³/L_{RV}, more preferably in the range from 30 to 200 cm³/L_{RV},

- 5 The micropore volume of the charge of porous particles in step (a) is preferably in the range from 15 to 180 cm³/L_{RV}, more preferably from 20 to 160 cm³/L_{RV}, more preferably from 25 to 140 cm³/L_{RV}, more preferably from 30 to 120 cm³/L_{RV}, more preferably from 35 to 110 cm³/L_{RV}, more preferably from 40 to 100 cm³/L_{RV}, more preferably from 45 to 90 cm³/L_{RV}, more preferably from 50 to 80 cm³/L_{RV}.
- 10 Nitrogen gas adsorption is effective for the measurement of pore volume and pore size distributions for pores having a diameter up to 50 nm, but is less reliable for pores of much larger diameter. For the purposes of the present invention, nitrogen adsorption is therefore used to determine pore volumes and pore size distributions only for pores having a diameter up to and including 50 nm (i.e. only for micropores and mesopores). PD₅₀ are likewise
- 15 determined relative to the total volume of micropores and mesopores only.

- In view of the limitations of available analytical techniques it is not possible to measure pore volumes and pore size distributions across the entire range of micropores, mesopores and macropores using a single technique. In the case that the porous particles comprise macropores, the volume of pores having diameter in the range from greater than 50 nm and
- 20 up to 100 nm may be measured by mercury porosimetry and is preferably no more than 0.3 cm³/g, or no more than 0.20 cm³/g, or no more than 0.1 cm³/g, or no more than 0.05 cm³/g. A small fraction of macropores may be useful to facilitate electrolyte access into the pore network, but the advantages of the invention are obtained substantially by accommodating silicon in micropores and smaller mesopores.

- 25 Any pore volume measured by mercury porosimetry at pore sizes of 50 nm or below is disregarded (as set out above, nitrogen adsorption is used to characterize the mesopores and micropores). Pore volume measured by mercury porosimetry above 100 nm is assumed for the purposes of the invention to be inter-particle porosity and is also disregarded.
- 30 Mercury porosimetry is a technique that characterizes the porosity and pore diameter distributions of a material by applying varying levels of pressure to a sample of the material immersed in mercury. The pressure required to intrude mercury into the pores of the sample

is inversely proportional to the size of the pores. Values obtained by mercury porosimetry as reported herein are obtained in accordance with ASTM UOP578-11, with the surface tension γ taken to be 480 mN/m and the contact angle ϕ taken to be 140° for mercury at room temperature. The density of mercury is taken to be 13.5462 g/cm^3 at room temperature. A number of high precision mercury porosimetry instruments are commercially available, such as the AutoPore IV series of automated mercury porosimeters available from Micromeritics Instrument Corporation, USA. For a complete review of mercury porosimetry reference may be made to P.A. Webb and C. Orr in "Analytical Methods in Fine Particle Technology, 1997, Micromeritics Instrument Corporation, ISBN 0-9656783-0.

It will be appreciated that intrusion techniques such as gas adsorption and mercury porosimetry are effective only to determine the pore volume of pores that are accessible to nitrogen or to mercury from the exterior of the porous particles. Porosity values specified herein shall be understood as referring to the volume of open pores, i.e. pores that are accessible to a fluid from the exterior of the porous particles. Fully enclosed pores which cannot be identified by nitrogen adsorption or mercury porosimetry shall not be taken into account herein when determining porosity values. Likewise, any pore volume located in pores that are so small as to be below the limit of detection by nitrogen adsorption is not taken into account.

The term "particle diameter" as used herein refers to the equivalent spherical diameter (esd), i.e. the diameter of a sphere having the same volume as a given particle, wherein the particle volume is understood to include the volume of any intra-particle pores. The terms " D_{50} " and " D_{50} particle diameter" as used herein refer to the volume-based median particle diameter, i.e. the diameter below which 50% by volume of the particle population is found.

The terms " D_{10} " and " D_{10} particle diameter" as used herein refer to the 10th percentile volume-based median particle diameter, i.e. the diameter below which 10% by volume of the particle population is found. The terms " D_{90} " and " D_{90} particle diameter" as used herein refer to the 90th percentile volume-based median particle diameter, i.e. the diameter below which 90% by volume of the particle population is found.

Particle diameters and particle size distributions can be determined by standard laser diffraction techniques in accordance with ISO 13320:2009. Laser diffraction relies on the principle that a particle will scatter light at an angle that varies depending on the size the particle and a collection of particles will produce a pattern of scattered light defined by

intensity and angle that can be correlated to a particle size distribution. A number of laser diffraction instruments are commercially available for the rapid and reliable determination of particle size distributions. Unless stated otherwise, particle size distribution measurements as specified or reported herein are as measured by the conventional Malvern Mastersizer™ 3000 particle size analyzer from Malvern Instruments™. The Malvern Mastersizer™ 3000 particle size analyzer operates by projecting a helium-neon gas laser beam through a transparent cell containing the particles of interest suspended in an aqueous solution. Light rays which strike the particles are scattered through angles which are inversely proportional to the particle size and a photodetector array measures the intensity of light at several predetermined angles and the measured intensities at different angles are processed by a computer using standard theoretical principles to determine the particle size distribution. Laser diffraction values as reported herein are obtained using a wet dispersion of the particles in 2-propanol with a 5 vol% addition of the surfactant SPAN™-40 (sorbitan monopalmitate). The particle refractive index is taken to be 2.68 for porous particles and 3.50 for composite particles and the dispersant index is taken to be 1.378. Particle size distributions are calculated using the Mie scattering model.

In general, the porous particles may have a D_{50} particle diameter in the range from 0.5 to 200 μm . Preferably, the D_{50} particle diameter of the porous particles may be at least 1 μm , or at least 1.5 μm , or at least 2 μm , or at least 2.5 μm , or at least 3 μm , or at least 4 μm , or at least 5 μm , or at least 6 μm . Optionally the D_{50} particle diameter of the porous particles may be no more than 150 μm , or no more than 100 μm , or no more than 70 μm , or no more than 50 μm , or no more than 40 μm , or no more than 30 μm , or no more than 25 μm , or no more than 20 μm , or no more than 18 μm , or no more than 15 μm , or no more than 12 μm , or no more than 10 μm , or no more than 8 μm .

For instance, the porous particles may have a D_{50} particle diameter in the range from 0.5 to 150 μm , or from 0.5 to 100 μm , or from 0.5 to 50 μm , or from 0.5 to 30 μm , or from 1 to 25 μm , or from 1 to 20 μm , or from 2 to 25 μm , or from 2 to 20 μm , or from 2 to 18 μm , or from 2 to 15 μm , or from 2 to 12 μm , or from 2.5 to 15 μm , or from 2.5 to 12 μm , or from 2 to 10 μm , or from 3 to 20 μm , or from 3 to 18 μm , or from 3 to 15 μm , or from 4 to 18 μm , or from 4 to 15 μm , or from 4 to 12 μm , or from 5 to 15 μm , or from 5 to 12 μm or from 5 to 10 μm , or from 5 to 8 μm . Particles within these size ranges and having porosity and a pore diameter distribution as set out herein are ideally suited for the preparation of composite particles for use in anodes for metal-ion batteries by a CVI process.

The D_{10} particle diameter of the porous particles is preferably at least $0.2\text{ }\mu\text{m}$, or at least $0.5\text{ }\mu\text{m}$, or at least $0.8\text{ }\mu\text{m}$, or at least $1\text{ }\mu\text{m}$, or at least $1.5\text{ }\mu\text{m}$, or at least $2\text{ }\mu\text{m}$. By maintaining the D_{10} particle diameter at $0.2\text{ }\mu\text{m}$ or more, the potential for undesirable agglomeration of sub-micron sized particles is reduced, and improved dispersibility of the composite particles formed.

The D_{90} particle diameter of the porous particles is preferably no more than $300\text{ }\mu\text{m}$, or no more than $250\text{ }\mu\text{m}$, or no more than $200\text{ }\mu\text{m}$, or no more than $150\text{ }\mu\text{m}$, or no more than $100\text{ }\mu\text{m}$, or no more than $80\text{ }\mu\text{m}$, or no more than $60\text{ }\mu\text{m}$, or no more than $40\text{ }\mu\text{m}$, or no more than $30\text{ }\mu\text{m}$, or no more than $25\text{ }\mu\text{m}$, or no more than $20\text{ }\mu\text{m}$.

Preferably, the D_1 particle diameter of the porous particles is at least $0.8\text{ }\mu\text{m}$, or at least $1.0\text{ }\mu\text{m}$, or at least $1.2\text{ }\mu\text{m}$, or at least $1.4\text{ }\mu\text{m}$, or at least $1.5\text{ }\mu\text{m}$, or at least $1.6\text{ }\mu\text{m}$, or at least $1.8\text{ }\mu\text{m}$, or at least $2.0\text{ }\mu\text{m}$, or at least $2.2\text{ }\mu\text{m}$, or at least $2.4\text{ }\mu\text{m}$, or at least $2.5\text{ }\mu\text{m}$, or at least $2.6\text{ }\mu\text{m}$, or at least $2.8\text{ }\mu\text{m}$, or at least $3.0\text{ }\mu\text{m}$. It will be appreciated that the D_1 particle diameter of the porous particles provides a measure of the content of fine particles in the charge of porous particles. It has been found that substantially eliminating fines from the porous particles provides for improved deposition of silicon, in particular by increasing the content of "surface silicon" in the composite particles. The "surface silicon" content of the composite particles is discussed in further detail below.

Preferably, the D_1 particle diameter is in the range from 1.5 to $4.5\text{ }\mu\text{m}$, or from 2 to $4\text{ }\mu\text{m}$, or from 2.5 to $3.5\text{ }\mu\text{m}$, or from 11 to $13\text{ }\mu\text{m}$.

The deposition of electroactive materials into porous particles that are excessively large may be less efficient due to the longer distance that precursor molecules must diffuse through the pore structure to reach the innermost pores. Deposition of the electroactive material in pores nearer to the particle surface can obstruct access of the precursor molecules to the innermost pores, resulting in particles that are underfilled and thus non-homogenous deposition of the electroactive material between particles of different sizes. Outsize particles also pack less efficiently and therefore obstruct the formation of electrode layers of homogenous structure and composition.

Accordingly, the D_{90} particle diameter of the porous particles is preferably no more than $30\text{ }\mu\text{m}$, or no more than $25\text{ }\mu\text{m}$, or no more than $20\text{ }\mu\text{m}$, or no more than $18\text{ }\mu\text{m}$, or no more than $15\text{ }\mu\text{m}$, or no more than $12\text{ }\mu\text{m}$.

The D_{98} particle diameter of the porous particles is preferably no more than 35 μm , or no more than 30 μm , or no more than 25 μm , or no more than 20 μm , or no more than 18 μm , or no more than 16 μm .

5 The D_{100} particle diameter of the porous particles is preferably no more than 40 μm , or no more than 35 μm , or no more than 30 μm , or no more than 25 μm , or no more than 20 μm .

Preferably, the difference between the D_{98} particle diameter and the D_1 particle diameter of the porous particles ($D_{98}-D_1$) is no more than 18 μm , or no more than 16 μm , or no more than 15 μm , or no more than 14 μm , or no more than 13 μm , or no more than 12 μm .

10 Preferably, the ratio of the D_{98} particle diameter to the D_1 particle diameter of the porous particles (D_{98}/D_1) is no more than 12, or no more than 10, or no more than 8, or no more than 6, or no more than 5.

Preferably, $(D_{98}-D_1)/D_{50}$ is no more than 2.2, or no more than 2, or no more than 1.9, or no more than 1.8, or no more than 1.7, or no more than 1.6.

15 The porous particles may have an average sphericity (as defined herein) of more than 0.5. Preferably they have an average sphericity of at least 0.55, or at least 0.6, or at least 0.65, or at least 0.7, or at least 0.75, or at least 0.8, or at least 0.85. Spherical particles are believed to aid uniformity of deposition and facilitate denser packing of particles, both in continuous reactors and of the final product when incorporated into electrodes.

20 It is possible to obtain highly accurate two-dimensional projections of micron scale particles by scanning electron microscopy (SEM) or by dynamic image analysis, in which a digital camera is used to record the shadow projected by a particle. The term "sphericity" as used herein shall be understood as the ratio of the area of the particle projection (obtained from such imaging techniques) to the area of a circle, wherein the particle projection and circle have identical circumference. Thus, for an individual particle, the sphericity S may be defined as:

$$S = \frac{4 \cdot \pi \cdot A_m}{(C_m)^2}$$

wherein A_m is the measured area of the particle projection and C_m is the measured circumference of the particle projection. The average sphericity S_{av} of a population of particles as used herein is defined as:

16

$$S_{av} = \frac{1}{n} \sum_{i=1}^n \left[\frac{4 \cdot \pi \cdot A_m}{(C_m)^2} \right]$$

wherein n represents the number of particles in the population. The average sphericity for a population of particles is preferably calculated from the two-dimensional projections of at least 50 particles.

- 5 The porous particles are preferably porous conductive particles. A preferred type of porous conductive particles is porous carbon particles. The porous carbon particles preferably comprise at least 80 wt% carbon, more preferably at least 90 wt% carbon, more preferably at least 95 wt% carbon, and optionally at least 98wt% or at least 99 wt% carbon. The carbon may be crystalline carbon or amorphous carbon, or a mixture of amorphous and
10 crystalline carbon. The porous carbon particles may be either hard carbon particles or soft carbon particles.

- As used herein, the term “hard carbon” refers to a disordered carbon matrix in which carbon atoms are found predominantly in the sp^2 hybridised state (trigonal bonds) in nanoscale polyaromatic domains. The polyaromatic domains are cross-linked with a chemical bond,
15 e.g. a C-O-C bond. Due to the chemical cross-linking between the polyaromatic domains, hard carbons cannot be converted to graphite at high temperatures. Hard carbons have graphite-like character as evidenced by the large G-band ($\sim 1600 \text{ cm}^{-1}$) in the Raman spectrum. However, the carbon is not fully graphitic as evidenced by the significant D-band ($\sim 1350 \text{ cm}^{-1}$) in the Raman spectrum. The graphitic nature of carbon materials can be
20 assessed by monitoring the ratio in peak intensity of the D-band to the G-band (ID/IG). The porous carbon particles may comprise an ID/IG of no more than 1.8, or no more than 1.6, or no more than 1.4, or no more than 1.2, or no more than 1, or no more than 0.84, or no more than 0.75.

- As used herein, the term “soft carbon” also refers to a disordered carbon matrix in which
25 carbon atoms are found predominantly in the sp^2 hybridised state (trigonal bonds) in polyaromatic domains having dimensions in the range from 5 to 200 nm. In contrast to hard carbons, the polyaromatic domains in soft carbons are associated by intermolecular forces but are not cross-linked with a chemical bond. This means that they will graphitise at high temperature. The porous carbon particles preferably comprise at least 50% sp^2 hybridised
30 carbon as measured by XPS. For example, the porous carbon particles may suitably

comprise from 50% to 98% sp^2 hybridised carbon, from 55% to 95% sp^2 hybridised carbon, from 60% to 90% sp^2 hybridised carbon, or from 70% to 85% sp^2 hybridised carbon.

A variety of different materials may be used to prepare suitable porous carbon frameworks. Examples of organic materials that may be used include plant biomass including lignocellulosic materials (such as coconut shells, rice husks, wood etc.) and fossil carbon sources such as coal. Examples of resins and polymeric materials which form porous carbon particles on pyrolysis include phenolic resins, novolac resins, pitch, melamines, polyacrylates, polystyrenes, polyvinylalcohol (PVA), polyvinylpyrrolidone (PVP), and various copolymers comprising monomer units of acrylates, styrenes, α -olefins, vinyl pyrrolidone and other ethylenically unsaturated monomers. A variety of different carbon materials are available in the art depending on the starting material and the conditions of the pyrolysis process. Porous carbon particles of various different specifications are available from commercial suppliers.

The porous carbon particles may undergo a chemical or gaseous activation process to increase the volume of mesopores and micropores. A suitable activation process comprises contacting pyrolyzed carbon with one or more of oxygen, steam, CO, CO₂ and KOH at a temperature in the range from 600 to 1000 °C.

Mesopores can also be obtained by known templating processes, using extractable pore formers such as MgO and other colloidal or polymer templates which can be removed by thermal or chemical means post pyrolysis or activation.

Alternatives to carbon-based conductive particles include porous metal oxides, such as oxides of titanium having the formula TiO_x where x has a value greater than 1 and less than 2.

The porous particles preferably have a BET surface area of at least 750 m²/g, or at least 1,000 m²/g, or at least 1,250 m²/g, or at least 1,500 m²/g, or at least 1,600 m²/g. Preferably, the BET surface area of the porous particles is no more than 4,000 m²/g, or no more than 3,500 m²/g, or no more than 3,250 m²/g, or no more than 3,000 m²/g or no more than 2,500 m²/g, or no more than 2,000 m²/g, or no more than 1,800 m²/g. For example, the porous particles may have a BET surface area in the range from 750 m²/g to 4,000 m²/g, or from 1,000 m²/g to 3,500 m²/g, or from 1,250 m²/g to 3,250 m²/g, or from 1,500 m²/g to 3,000 m²/g.

Preferred porous particles for use according to the invention include those in which:

- (i) the D_{50} particle diameter is in the range from 0.5 to 30 μm ;
- (ii) the total pore volume of micropores and mesopores as measured by gas adsorption is in the range from 0.5 to 1.5 cm^3/g ;
- 5 (iii) the PD_{50} pore diameter as measured by gas adsorption is no more than 5 nm;

Preferred porous particles for use according to the invention include those in which:

- (i) the total pore volume of micropores and mesopores as measured by gas adsorption is in the range from 0.65 to 0.9 cm^3/g ;
- 10 (ii) the BET surface area is from 1600 to 1800 m^2/g ;
- (iii) the PD_{50} pore diameter as measured by gas adsorption is no more than 2 nm;
- (iv) the charge of porous particles in step (a) has a total micropore volume as measured by gas adsorption of from 70 to 100 $\text{cm}^3/\text{L}_{\text{RV}}$.

Preferred porous particles for use according to the invention include those in which:

- 15 (i) the total pore volume of micropores and mesopores as measured by gas adsorption is in the range from 0.65 to 0.9 cm^3/g ;
- (ii) the BET surface area is from 1600 to 1800 m^2/g ;
- (iii) the PD_{50} pore diameter as measured by gas adsorption is no more than 2 nm;
- (iv) the charge of porous particles in step (a) has a total micropore volume as measured
20 by gas adsorption of from 70 to 100 $\text{cm}^3/\text{L}_{\text{RV}}$;
- (v) the D_{50} particle diameter is in the range from 6 to 8 μm .

Optionally, the charge of porous particles in the pressure reactor is flushed with an inert gas prior to step (b). Optionally, the charge of porous particles is heated to the CVI reaction temperature under a flow of inert gas and deposition of silicon is initiated by switching the
25 inert gas for the silicon precursor gas.

Optionally, the charge of porous particles is pre-heated before it is introduced into the pressure reactor. Preferably, the charge of porous particles is pre-heated to a temperature

that is $\geq(T_{RZ} - 200)$ °C, wherein T_{RZ} is the reaction temperature of the pressure reactor in step (b), preferably to a temperature that is $\geq(T_{RZ} - 100)$ °C, more preferably to a temperature that is $\geq(T_{RZ} - 50)$ °C.

The process of the invention further preferably comprises controlling the flow rate of the silicon precursor gas into the pressure reactor in proportion to the total surface area of the porous particles. Preferably, the flow rate of the silicon precursor gas into the pressure reactor in grams of silicon per m² of porous particle surface area per minute in step (b) is at least 3×10^{-7} g_{Si}/m²/min, more preferably at least 4×10^{-7} g_{Si}/m²/min, more preferably at least 5×10^{-7} g_{Si}/m²/min, more preferably at least 6×10^{-7} g_{Si}/m²/min, more preferably at least 8×10^{-7} g_{Si}/m²/min, more preferably at least 1.0×10^{-6} g_{Si}/m²/min, more preferably at least 1.2×10^{-6} g_{Si}/m²/min, more preferably at least 1.5×10^{-6} g_{Si}/m²/min, more preferably at least 2.0×10^{-6} g_{Si}/m²/min.

For completeness, the flow rate of silicon the silicon precursor is quantified based on the mass of silicon contained therein. For example, in the case that the silicon precursor is silane (SiH₄), the mass of silicon supplied to the reactor is 87.34% of the mass of silane supplied.

Preferably, the flow rate of the silicon precursor gas into the pressure reactor in grams of silicon (g_{Si}) per m² of porous particle surface area per minute in step (b) is 5.0×10^{-5} g_{Si}/m²/min, more preferably no more than 2.5×10^{-5} g_{Si}/m²/min, more preferably no more than 2.0×10^{-5} g_{Si}/m²/min, more preferably no more than 1.5×10^{-5} g_{Si}/m²/min, more preferably no more than 1.0×10^{-5} g_{Si}/m²/min, more preferably no more than 8.0×10^{-6} g_{Si}/m²/min, more preferably no more than 6.0×10^{-6} g_{Si}/m²/min, more preferably no more than 5.0×10^{-6} g_{Si}/m²/min, more preferably no more than 4.0×10^{-6} g_{Si}/m²/min, more preferably no more than 3.0×10^{-6} g_{Si}/m²/min.

Preferably, the the flow rate of the silicon precursor gas into the pressure reactor in grams of silicon (g_{Si}) per m² of porous particle surface area per minute in step (b) is in the range from 3×10^{-7} to 5.0×10^{-5} g_{Si}/m²/min, more preferably from 4×10^{-7} to 2.5×10^{-5} g_{Si}/m²/min, more preferably from 5×10^{-7} to 2.0×10^{-5} g_{Si}/m²/min, more preferably from 6×10^{-7} to 1.5×10^{-5} g_{Si}/m²/min, more preferably from 8×10^{-7} to 1.0×10^{-5} g_{Si}/m²/min, more preferably from 1.0×10^{-6} to 8.0×10^{-6} g_{Si}/m²/min, more preferably from 1.2×10^{-6} to 6.0×10^{-6} g_{Si}/m²/min, more preferably from 1.5×10^{-6} to 5.0×10^{-6} g_{Si}/m²/min, more preferably from 2.0×10^{-6} to 4.0×10^{-6} g_{Si}/m²/min.

The process of the invention is particularly well-adapted to operation at manufacturing scale since inhomogeneities within a reaction vessel increase with the scale of reaction, in particular since the average diffusion distances for the silicon precursor gas are greater than in a laboratory scale process. Accordingly, the process of the invention is preferably carried out at scale. Preferably, the charge of porous particles in step (a) is at least 500 g, more preferably at least 1 kg, more preferably at least 2 kg, more preferably at least 5 kg, more preferably at least 10 kg, more preferably at least 15 kg, more preferably at least 20 kg, more preferably at least 30 kg, more preferably at least 40 kg, more preferably at least 50 kg. For example the charge of porous particles in step (a) may be at least 100 kg, or at least 200 kg, or at least 500 kg, or at least 1,000 kg, or at least 5,000 kg, or at least 10,000 kg.

Step (b) preferably step (b) comprises continuously agitating the porous particles. Preferably step (b) comprises mechanically agitating the porous particles. Preferably, step (b) comprises continuously mechanically agitating the porous particles. Preferably, step (b) comprises continuously mechanically fluidising the porous particles.

Preferably the pressure reactor comprises an agitator for agitating the porous particles during said contacting. Any suitable agitator may be used, such as a turbine agitator, a paddle agitator, an anchor agitator, a propeller agitator, or a helical agitator.

Mechanically agitating the porous particles decouples the silicon precursor gas supply from agitation of the porous particles. With a fluidised bed reactor, agitation of the porous particles can only be achieved by supplying the silicon precursor gas at a sufficient velocity to fluidise the porous particles. In consequence, the use of mechanical agitation enables the process to function with lower silicon precursor gas velocity than fluidised bed reactor processes and allows the flow rate of the silicon precursor to be adjusted independently from agitation.

Continuous mechanical agitation allows increased porous particle loading per litre of the reactor whilst maintaining homogenous silicon deposition. In technologies reliant on a relatively high ratio of reactor surface area to mass of porous particles, a temperature gradient exists across the porous particle bed thickness, thus limiting the effective porous particle bed thickness at which the silicon infiltration is homogenous. As a result, the maximum powder bed thickness and porous particle loading is limited. In a continuously mechanically agitated system, the continuous movement and recirculation of the porous

particles within the reactor allows for a higher quantity of porous particles to contact the reactor surface, homogeneity of heat transfer is improved, and the porous particles have a reduced temperature gradient. This allows for a greater porous particle loading per reactor volume.

- 5 The temperature in the pressure reactor during step (b) is preferably in the range from 340 to 500 °C, or from 350 to 500 °C, or from 350 to 480 °C, or from 350 to 450 °C, or from 350 to 420 °C, or from 340 to 400 °C, or from 340 to 395 °C, or from 340 to 390 °C, or from 345 to 400 °C, or from 345 to 395 °C, or from 345 to 390 °C, or from 350 to 400 °C, or from 350 to 395 °C, or from 350 to 390 °C, or from 350 to 385 °C, or from 350 to 380 °C, or from 355 to 400 °C, or from 355 to 395 °C, or from 355 to 390 °C, or from 355 to 385 °C, or from 355 to 380 °C, or from 360 to 400 °C, or from 360 to 395 °C, or from 360 to 390 °C, or from 360 to 385 °C, or from 360 to 380 °C, or from 365 to 400 °C, or from 365 to 395 °C, or from 365 to 390 °C, or from 365 to 385 °C, or from 365 to 380 °C, or from 370 to 400 °C, or from 370 to 395 °C, or from 370 to 390 °C, or from 370 to 385 °C, or from 370 to 380 °C, or from 375 to 385 °C. Operation at greater temperatures in the pressure reactor will increase the rate of the reaction and lead to faster deposition rate.

- The temperature in the pressure reactor during step (b) is preferably at least 340 °C, more preferably at least 350 °C, more at least 355 °C, more at least 360 °C. The temperature in the pressure reactor during step (b) is preferably no more than 500 °C, more preferably no more than 480 °C, more preferably no more than 450 °C, more preferably no more than 420 °C, more preferably no more than 400 °C, more preferably no more than 395 °C, more preferably no more than 390 °C, more preferably no more than 385 °C, more preferably no more than 380 °C.

- The process of the invention is preferably operated under a regime where the silicon precursor is supplied to the pressure reactor at high concentration, or even in neat form. In order to control the rate of reaction and to achieve controlled infiltration of the silicon precursor into the pore network of the porous particles, the reaction temperature in the pressure reactor is preferably no more than 420 °C, more preferably no more than 410 °C, more preferably no more than 400 °C, more preferably no more than 395 °C. A temperature range of from 370 to 395 °C is particularly preferred.

The conditions in step (b) preferably include a pressure of at least 50 kPa, or at least 100 kPa, or at least 150 kPa, or at least 200 kPa, or at least 250 kPa, or at least 300 kPa, or at least 400 kPa, or at least 500 kPa, or at least 600 kPa.

5 The conditions in step (b) preferably include a pressure of no more than 5,000 kPa, or no more than 2,000 kPa, or no more than 1,800 kPa, or no more than 1,600 kPa, or no more than 1,500 kPa, or no more than 1,200 kPa, or no more than 1,100 kPa, or no more than 1,000 kPa, or no more than 900 kPa, or no more than 800 kPa.

10 The conditions in step (b) preferably include a pressure in the range from 50 to 5,000 kPa, or from 50 to 2,000 kPa, or from 100 to 2,000 kPa, or from 120 to 1,800 kPa, or from 150 to 1,600 kPa, or from 200 to 1,500 kPa, or from 250 to 1,200 kPa, or from 300 to 1,100 kPa, or from 400 to 1000 kPa, or from 500 to 900 kPa, or from 600 to 800 kPa. All pressure values disclosed herein are absolute pressures unless specified otherwise.

15 Operation at elevated pressure has the advantage that mass transfer limitations on the reaction rate are reduced, facilitating infiltration of the silicon precursor gas into the pore network of the porous particles. Operating at greater pressures also increases the residence time of the silicon precursor gas, thus increasing conversion of the silicon precursor. Operation at too great a pressure has the disadvantage that pressure negatively affects the thermodynamic equilibrium of silicon decomposition, thus limiting the extent of the reaction. Operation at a pressure below 700 kPa has the advantage that specialist
20 apparatus is not required, thus reducing costs.

To prevent uncontrolled reaction, lower reaction temperatures are used when the reactor is operated at high pressure. In particular, where the pressure in the pressure reactor is above 100 kPa, the reaction temperature in the pressure reactor is preferably no more than 450 °C, more preferably no more than 430 °C, more preferably no more than 420 °C, more
25 preferably no more than 410 °C, more preferably no more than 400 °C, more preferably no more than 395 °C.

Optionally, the temperature in the pressure reactor during step (b) is in the range from 340 to 500 °C and the pressure in the pressure reactor during step (b) is in the range from 600 to 5000 kPa.

Optionally, the temperature in the pressure reactor during step (b) is in the range from 360 to 390 °C and the pressure in the pressure reactor during step (b) is in the range from 600 to 2000 kPa.

5 Optionally, the temperature in the pressure reactor during step (b) is in the range from 360 to 385 °C and the pressure in the pressure reactor during step (b) is in the range from 700 to 2000 kPa.

Optionally, the temperature in the pressure reactor during step (b) is in the range from 360 to 380 °C and the pressure in the pressure reactor during step (b) is in the range from 1000 to 2000 kPa.

10 The partial pressure of the silicon precursor in the pressure reactor during step (b) is preferably at least 10 kPa, or at least 20 kPa, or at least 30 kPa, or at least 40 kPa, or at least 50 kPa, or at least 60 kPa, or at least 70 kPa, or at least 80 kPa, or at least 90 kPa, or at least 100 kPa, or at least 105 kPa, or at least 110 kPa, or at least 115 kPa, or at least 120 kPa, or at least 150 kPa, or at least 200 kPa, or at least 250 kPa, or at least 300 kPa,
15 or at least 400 kPa, or at least 500 kPa, or at least 600 kPa.

The partial pressure of the silicon precursor in the pressure reactor during step (b) is preferably no more than 5000 kPa, or no more than 2000 kPa, or no more than 1600 kPa, or no more than 1500 kPa, or no more than 1200 kPa, or no more than 1000 kPa, or no more than 900 kPa, or no more than 800 kPa.

20 Optionally, the silicon precursor gas is pre-heated before it is introduced into the pressure reactor. Preferably, the silicon precursor gas is pre-heated to a temperature that is $\geq(T_{RZ} - 200)$ °C, wherein T_{RZ} is the reaction temperature of the pressure reactor, preferably to a temperature that is $\geq(T_{RZ} - 100)$ °C, more preferably to a temperature that is $\geq(T_{RZ} - 50)$ °C.

25 Step (b) preferably comprises continuously or semi-continuously withdrawing an effluent gas from the pressure reactor.

The effluent gas from the pressure reactor comprises at least one by-product gas from the CVI reaction and optionally unreacted silicon precursor. The effluent gas may comprise silicon precursor, at least one byproduct gas and optionally other gases such as hydrogen
30 or an inert gas, such as nitrogen or argon. The effluent gas may comprise from 2.5 to 80 vol% of the silicon precursor, or from 2.5 to 70 vol%, or from 2.5 to 60 vol%, or from 2.5 to

50 vol%, or from 5 to 80 vol %, or from 5 to 70 vol%, or from 5 to 60 vol%, or from 5 to 50 vol% of the silicon precursor. Controlling the pressure reactor such that the effluent gas comprises unreacted silicon precursor may be preferable as it ensures that a high concentration of silicon precursor can be maintained throughout the pressure reactor. In

the case that the effluent gas from the pressure reactor contains significant quantities of unreacted silicon precursor, it may be appropriate to recover the unreacted silicon precursor from the effluent gas and to recycle the recovered silicon precursor to the pressure reactor. Means of recovering the unreacted silicon precursor from the effluent gas include semi-permeable membrane separation processes, pressure-swing absorption processes, and cryogenic separation processes.

Optionally, the pressure reactor may comprise more than one outlet for the effluent gas. The use of multiple outlets for the gas provides for a further improvement in the gas flow dynamics within the pressure reactor. This is particularly useful in the case that the process is carried out on a large scale as set out above.

15 The flow rate of the silicon precursor may be kept at a single throughout the duration of step (b) or it may be varied within the defined ranges over the duration of step (b).

Step (b) may optionally comprise adjusting the flow rate of the silicon precursor into the pressure reactor from an initial flow rate to an adjusted flow rate, wherein the adjusted flow rate is less than the initial flow rate. For example, the flow rate of the silicon precursor may be reduced in response to a reduced rate of reaction as the deposition of silicon proceeds. It will be understood that the deposition of silicon has the effect of reducing the surface area of the porous particles and therefore the rate of reaction will generally decrease as the deposition proceeds, assuming all other reaction variables are kept constant.

Optionally, the adjusted flow rate of the silicon precursor may be no more than 90% or no more than 80% or no more than 70%, or no more than 60% or no more than 50% of an initial flow rate.

For example, step (b) may contain a first reaction phase in which the flow rate of the silicon precursor is maintained at an essentially constant initial flow rate and a second reaction phase in which the flow rate of the silicon precursor is adjusted to an adjusted flow rate.

30 Optionally, the flow rate of the silicon precursor is adjusted after at least 15 %, or at least
20 %, or at least 25 %, or at least 30 %, or at least 35 %, or at least 40 %, or at least 45 %,

or at least 50 %, or at least 55 %, or at least 60 %, or at least 65 %, or at least 70 %, or at least 75 %, or at least 80 %, or at least 85 %, or at least 90 % of the target silicon content by mass has been introduced into the reactor in the form of the silicon precursor gas.

Step (b) may optionally comprise adjusting the internal pressure of the pressure reactor
5 from an initial pressure to an adjusted pressure, wherein the adjusted pressure is greater than the initial pressure. Again, the internal pressure of the pressure reactor may be increased in response to a reduced rate of reaction as the deposition of silicon proceeds.

Optionally, the adjusted pressure is at least 10%, or at least 20, or at least 30%, or at least 40%, or at least 50%, or at least 60 %, or at least 70 %, or at least 80 %, or at least 90 %,
10 or at least 100 %, or at least 200%, or at least 500%, or at least 1,000% higher than the initial pressure.

For example, step (b) may contain a first reaction phase in which the internal pressure of the pressure reactor is maintained at an essentially constant initial pressure and a second reaction phase in which the internal pressure of the pressure reactor is adjusted to an
15 adjusted pressure.

Optionally, the internal pressure of the pressure reactor is adjusted after at least 15 %, or at least 20 %, or at least 25 %, or at least 30 %, or at least 35 %, or at least 40 %, or at least 45 %, or at least 50 %, or at least 55 %, or at least 60 %, or at least 65 %, or at least 70 %, or at least 75 %, or at least 80 %, or at least 85 %, or at least 90 % of the target silicon
20 content by mass has been introduced into the reactor in the form of the silicon precursor gas.

Optionally, step (b) may comprise monitoring the silicon precursor content of the effluent gas from the pressure reactor and adjusting the flow rate of the silicon precursor and/or the internal pressure of the pressure reactor in response to an increase in the silicon precursor
25 content of the effluent gas (this being indicative of a decrease in the reaction rate).

Optionally, the pressure reactor has an aspect ratio (defined herein as the ratio of maximum height to the maximum diameter of the internal reactor volume) in the range from 0.2 to 5, preferably from 0.3 to 3, more preferably from 0.5 to 2, more preferably from 0.75 to 1.5. A high aspect ratio is volumetrically efficient compared to prior art processes in which CVI is
30 typically carried out on a thin layer of porous particles in a static or agitated bed.

Taken in combination with the requirements set out herein for the surface area of the porous particles per litre of reactor volume, a pressure reactor aspect ratio of ca. 1 ensures that the mass of porous particles in the reactor itself has an aspect ratio of ca. 1 (i.e. such that the CVI process takes place with the porous particles in the bulk rather than in a thin layer. It has been found that the process conditions set out herein are particularly suited to reactions carried out using bulk porous particles, in which control of the diffusion of the silicon precursor within the reactor volume is particularly challenging.

Optionally, the process of the invention may be operated such that:

- (i) the charge of porous particles in step (a) has a total surface area of 8.0×10^4 to $1.0 \times 10^6 \text{ m}^2/\text{L}_{\text{RV}}$;
- (ii) the flow rate of the silicon precursor gas into the pressure reactor in step (b) is from 3×10^{-7} to $5.0 \times 10^{-5} \text{ g}_{\text{Si}}/\text{m}^2/\text{min}$;
- (iii) the temperature in the pressure reactor during step (b) is from 350 to 450 °C; and
- (iv) the pressure in the pressure reactor during step (b) is from 200 to 5,000 kPa.

Optionally, the process of the invention may be operated such that:

- (i) the charge of porous particles in step (a) has a total surface area of 1.0×10^5 to $8.0 \times 10^5 \text{ m}^2/\text{L}_{\text{RV}}$;
- (ii) the flow rate of the silicon precursor gas into the pressure reactor in step (b) is from 4×10^{-7} to $2.5 \times 10^{-5} \text{ g}_{\text{Si}}/\text{m}^2/\text{min}$;
- (iii) the temperature in the pressure reactor during step (b) is from 350 to 420 °C; and
- (iv) the pressure in the pressure reactor during step (b) is from 200 to 2,000 kPa.

Optionally, the process of the invention may be operated such that:

- (i) the charge of porous particles in step (a) has a total surface area of 1.5×10^5 to $6.0 \times 10^5 \text{ m}^2/\text{L}_{\text{RV}}$;
- (ii) the flow rate of the silicon precursor gas into the pressure reactor in step (b) is from 5×10^{-7} to $2.0 \times 10^{-5} \text{ g}_{\text{Si}}/\text{m}^2/\text{min}$;
- (iii) the temperature in the pressure reactor during step (b) is from 360 to 400 °C; and
- (iv) the pressure in the pressure reactor during step (b) is from 200 to 1,500 kPa.

Optionally, the process of the invention may be operated such that:

- (i) the charge of porous particles in step (a) has a total surface area of 2.0×10^5 to $5.0 \times 10^5 \text{ m}^2/\text{L}_{\text{RV}}$;
- (ii) the flow rate of the silicon precursor gas into the pressure reactor in step (b) is from 1.0×10^{-6} to $8.0 \times 10^{-6} \text{ g}_{\text{Si}}/\text{m}^2/\text{min}$;
- 5 (iii) the temperature in the pressure reactor during step (b) is from 365 to 400 °C; and
- (iv) the pressure in the pressure reactor during step (b) is from 250 to 1,200 kPa.

Optionally, the process of the invention may be operated such that:

- (i) the charge of porous particles in step (a) has a total surface area of 8.0×10^4 to $1.0 \times 10^6 \text{ m}^2/\text{L}_{\text{RV}}$;
- 10 (ii) the flow rate of the silicon precursor gas into the pressure reactor in step (b) is from 3×10^{-7} to $5.0 \times 10^{-5} \text{ g}_{\text{Si}}/\text{m}^2/\text{min}$;
- (iii) the temperature in the pressure reactor during step (b) is from 350 to 450 °C;
- 15 (iv) the pressure in the pressure reactor during step (b) is from 200 to 5,000 kPa;
- (v) the total pore volume of micropores and mesopores of the porous particles in step (a) is in the range from 0.5 to 1.5 cm^3/g ; and
- (vi) the PD_{50} pore diameter of the porous particles in step (a) is no more than 5 nm.

20 Optionally, the process of the invention may be operated such that:

- (i) the charge of porous particles in step (a) has a total surface area of 1.0×10^5 to $8.0 \times 10^5 \text{ m}^2/\text{L}_{\text{RV}}$;
- (ii) the flow rate of the silicon precursor gas into the pressure reactor in step (b) is from 4×10^{-7} to $2.5 \times 10^{-5} \text{ g}_{\text{Si}}/\text{m}^2/\text{min}$;
- 25 (iii) the temperature in the pressure reactor during step (b) is from 350 to 420 °C;
- (iv) the pressure in the pressure reactor during step (b) is from 200 to 2,000 kPa.
- (v) the total pore volume of micropores and mesopores of the porous particles in step (a) is in the range from 0.55 to 1.4 cm^3/g ; and
- 30 (vi) the PD_{50} pore diameter of the porous particles in step (a) is no more than 4 nm.

Optionally, the process of the invention may be operated such that:

- (i) the charge of porous particles in step (a) has a total surface area of 1.5×10^5 to $6.0 \times 10^5 \text{ m}^2/\text{L}_{\text{RV}}$;
- (ii) the flow rate of the silicon precursor gas into the pressure reactor in step (b) is from 5×10^{-7} to $2.0 \times 10^{-5} \text{ g}_{\text{Si}}/\text{m}^2/\text{min}$;
- 5 (iii) the temperature in the pressure reactor during step (b) is from 360 to 400 °C;
- (iv) the pressure in the pressure reactor during step (b) is from 200 to 1,500 kPa;
- (v) the total pore volume of micropores and mesopores of the porous particles in step (a) is in the range from 0.6 to 1.2 cm^3/g ; and
- 10 (vi) the PD_{50} pore diameter of the porous particles in step (a) is no more than 3 nm.

Optionally, the process of the invention may be operated such that:

- (i) the charge of porous particles in step (a) has a total surface area of 2.0×10^5 to $5.0 \times 10^5 \text{ m}^2/\text{L}_{\text{RV}}$;
- 15 (ii) the flow rate of the silicon precursor gas into the pressure reactor in step (b) is from 1.0×10^{-6} to $8.0 \times 10^{-6} \text{ g}_{\text{Si}}/\text{m}^2/\text{min}$;
- (iii) the temperature in the pressure reactor during step (b) is from 365 to 400 °C;
- (iv) the pressure in the pressure reactor during step (b) is from 250 to 1,200 kPa;
- 20 (v) the total pore volume of micropores and mesopores of the porous particles in step (a) is in the range from 0.6 to 1.0 cm^3/g ; and
- (vi) the PD_{50} pore diameter of the porous particles in step (a) is no more than 2.5 nm.

Optionally, the pressure reactor may comprise more than one inlet for the silicon precursor gas. The use of multiple inlets for the silicon precursor gas provides for a further improvement in the dispersion of the silicon precursor throughout the reactor volume and therefore throughout the mass of porous particles. This is particularly useful in the case that the process is carried out on a large scale as set out above.

The silicon precursor gas refers to a gas comprising a silicon compound or mixture of silicon compounds that is gaseous at the temperature of the CVI process and thermally decomposable to form elemental silicon and by-product gases. The silicon precursor gas optionally includes other gases, such as an inert gas. The portion of the gas composed of

decomposable silicon-containing compounds is referred to herein collectively as the silicon precursor.

- Examples of suitable silicon precursors include silane (SiH_4), disilane (Si_2H_6), trisilane (Si_3H_8), methylsilane, dimethylsilane and chlorosilanes, and mixtures thereof. Preferably,
- 5 the silicon precursor is selected from silane (SiH_4), disilane (Si_2H_6), trisilane (Si_3H_8), methylsilane and dimethylsilane. Silane (SiH_4) is the most preferred silicon precursor.

Preferably, the silicon precursor gas is free of chlorine, for example containing less than 1 wt%, preferably less than 0.1 wt%, preferably less than 0.01 wt% of chlorine-containing compounds.

- 10 The silicon precursor may be used undiluted (neat) or in a dilution such that the silicon precursor gas comprises at least 5 vol% of the silicon precursor and the balance of a gas selected from hydrogen and an inert gas, optionally wherein the inert gas is selected from nitrogen and argon.

- The silicon precursor gas preferably comprises at least 20 vol%, or at least 30 vol%, or at least 40 vol%, or at least 50 vol%, or at least 60 vol%, or at least 70 vol%, or at least 80 vol%, or at least 90 vol%, or at least 95 vol%, or at least 98 vol%, or at least 99 vol%, or at least 99.9 vol%, or at least 99.99 vol% of the silicon precursor. Preferably, the silicon precursor gas comprises at least 50 vol%, or at least 60 vol%, or at least 70 vol%, or at least 80 vol%, or at least 90 vol%, or at least 95 vol%, or at least 98 vol%, or at least 99 vol%, or at least 99.9 vol%, or at least 99.99 vol% of the silicon precursor. The vol% of silicon precursor refers to the concentration of silicon precursor as a proportion of the total gas (the silicon precursor gas) being introduced to the pressure reactor.
- 15
- 20

- The composite particles formed in step (b) may comprise at least 26 wt% silicon, or at least 28 wt% silicon, or at least 30 wt% silicon, or at least 32 wt% silicon, or at least 34 wt% silicon, or at least 36 wt% silicon, or at least 38 wt% silicon, or at least 40 wt% silicon, or at least 42 wt% silicon, or at least 44 wt% silicon.
- 25

The composite particles formed in step (b) may comprise no more than 62 wt% silicon, or no more than 60 wt% silicon, or no more than 58 wt% silicon, or no more than 56 wt% silicon, or no more than 54 wt% silicon.

- 30 The composite particles provided in step (b) preferably have a BET surface area of no more than $100 \text{ m}^2/\text{g}$, or no more than $80 \text{ m}^2/\text{g}$, or no more than $60 \text{ m}^2/\text{g}$, or no more than $40 \text{ m}^2/\text{g}$,

or no more than 30 m²/g, or no more than 25 m²/g, or no more than 20 m²/g, or no more than 15 m²/g, or no more than 10 m²/g. In general, a low BET surface area is preferred in order to minimize the formation of solid electrolyte interphase (SEI) layers at the surface of the composite particles during the first charge-discharge cycle of an anode. However, a

5 BET surface area which is excessively low results in unacceptably low charging rate and capacity due to the inaccessibility of the bulk of the electroactive material to metal ions in the surrounding electrolyte. For instance, the BET surface area of the composite particles is preferably at least 0.1 m²/g, or at least 1 m²/g, or at least 2 m²/g, or at least 5 m²/g. For instance, the BET surface area may be in the range from 0.1 to 100 m²/g, or from 0.1 to

10 80 m²/g, or from 0.5 to 60 m²/g, or from 0.5 to 40 m²/g, or from 1 to 30 m²/g, or from 1 to 25 m²/g, or from 2 to 20 m²/g. The term "BET surface area" as used herein should be taken to refer to the surface area per unit mass calculated from a measurement of the physical adsorption of gas molecules on a solid surface, using the Brunauer–Emmett–Teller theory, in accordance with ISO 9277.

15 The composite particles can be characterised by their performance under thermogravimetric analysis (TGA) in air. This method of analysis relies on the principle that a weight gain is observed when electroactive materials are oxidized in air and at elevated temperature.

As defined herein, "surface silicon" is calculated from the initial mass increase in the TGA

20 trace from a minimum between 150 °C and 500 °C to the maximum mass measured in the temperature range between 550 °C and 650 °C, wherein the TGA is carried out in air with a temperature ramp rate of 10 °C/min. This mass increase is assumed to result from the oxidation of surface silicon and therefore allows the percentage of surface silicon as a proportion of the total amount of silicon to be determined according to the following formula:

25
$$Y = 1.875 \times [(M_{\max} - M_{\min}) / M_f] \times 100\%$$

Wherein Y is the percentage of surface silicon as a proportion of the total silicon in the sample, M_{max} is the maximum mass of the sample measured in the temperature range between 550 °C to 650 °C, M_{min} is the minimum mass of the sample above 150 °C and below 500 °C, and M_f is the mass of the sample at completion of oxidation at 1400 °C. For

30 completeness, it will be understood that 1.875 is the molar mass ratio of SiO₂ to O₂ (i.e. the mass ratio of SiO₂ formed to the mass increase due to the addition of oxygen). Typically, the TGA analysis is carried out using a sample size of 10 mg ±2 mg.

It has been found that reversible capacity retention over multiple charge/discharge cycles is considerably improved when the surface silicon as determined by the TGA method described above is at least 20 wt% of the total amount of silicon in the material.

5 The composite particles provided in step (b) preferably comprise at least 20 wt% of the total amount of silicon as surface silicon. Or, at least 22 wt%, or at least 25 wt%, at least 30 wt% of the silicon, or at least 35 wt% of the silicon, or at least 40 wt% of the silicon, or at least 45 wt% of the silicon is surface silicon as determined by TGA.

10 The composite particles provided in step (b) preferably have a low content of coarse bulk silicon as determined by TGA. Coarse bulk silicon is defined herein as silicon which undergoes oxidation above 800 °C as determined by TGA, wherein the TGA is carried out in air with a temperature ramp rate of 10 °C/min. The coarse bulk silicon content is therefore determined according to the following formula:

$$Z = 1.875 \times [(M_f - M_{800}) / M_f] \times 100\%$$

15 Wherein Z is the percentage of unoxidized silicon at 800 °C, M_{800} is the mass of the sample at 800 °C, and M_f is the mass of ash at completion of oxidation at 1400 °C. For the purposes of this analysis, it is assumed that any mass increase above 800 °C corresponds to the oxidation of silicon to SiO_2 and that the total mass at completion of oxidation is SiO_2 . Typically, the TGA analysis is carried out using a sample size of 10 mg $\pm$ 2 mg.

20 Silicon that undergoes oxidation above 800 °C is less desirable. Preferably, no more than 10 wt%, or no more than 8 wt%, or no more than 6 wt%, or no more than 5 wt%, or no more than 4 wt%, or no more than 3 wt%, or no more than 2 wt%, or no more than 1.5 wt% of the silicon is coarse bulk silicon as determined by TGA.

25 Preferably, at least 20 wt% of the silicon is surface silicon and no more than 10 wt% of the silicon is coarse bulk silicon, wherein both are determined by TGA. More preferably, at least 30 wt% of the silicon is surface silicon and no more than 10 wt% of the silicon is coarse bulk silicon, wherein both are determined by TGA. More preferably, at least 35 wt% of the silicon is surface silicon and no more than 8 wt% of the silicon is coarse bulk silicon, wherein both are determined by TGA. More preferably, at least 40 wt% of the silicon is surface silicon and no more than 5 wt% of the silicon is coarse bulk silicon, wherein both are determined by TGA. More preferably, at least 45 wt% of the silicon is surface silicon and no more than 2 wt% of the silicon is coarse bulk silicon, wherein both are determined by TGA.

30

The process of the invention optionally further comprises the step of contacting the composite particles with a carbon precursor gas at conditions that are effective to cause deposition of carbon within the pores and/or on the surface of the composite particles.

- 5 The carbon deposited is a pyrolytic carbon material that is formed by the thermal decomposition of a carbon containing gas (such as ethylene). It provides a number of performance advantages. It reduces the BET surface area of the composite particles by smoothing any surface defects and filling any remaining surface microporosity, thereby further reducing first cycle loss. It also improves the conductivity of the surface of the composite particles, reducing the need for conductive additives in the electrode composition. In addition, it creates an optimum surface for the formation of a stable SEI layer, resulting in improved capacity retention on cycling.

- 15 Conditions that are effective to cause deposition of carbon may comprise a temperature in the range from 350 to 700 °C, or from 400 to 700 °C. Preferably, the temperature is no more than 680 °C, or no more than 660 °C, or no more than 640 °C, or no more than 620 °C, or no more than 600 °C, or no more than 580 °C, or no more than 560 °C, or no more than 540 °C, or no more than 520 °C, or no more than 500 °C.

- 20 The minimum temperature will depend on the type of carbon precursor that is used. Preferably, the temperature is at least 300 °C, or at least 350 °C, or at least 400 °C.

Conditions that are effective to cause deposition of carbon may comprise a pressure in the range from 1 to 600 kPa, or from 10 to 500 kPa, or from 20 to 200 kPa, or from 50 to 150 kPa, or from 80 to 120 kPa, or about 100 kPa.

- 25 Suitable carbon precursor gases include:
- (i) C₂-C₁₀ hydrocarbons, optionally wherein the hydrocarbons are selected from alkanes, alkenes, alkynes, cycloalkanes, cycloalkenes, and arenes, for example methane, ethylene, propylene, limonene, styrene, cyclohexane, cyclohexene, α-terpinene and acetylene;
 - 30 (ii) bicyclic monoterpenoids, optionally wherein the bicyclic monoterpenoids are selected from camphor, borneol, eucalyptol, camphene, carene, sabinene, thujene and pinene; and
 - (iii) polycyclic hydrocarbons comprising from 10 to 25 carbon atoms and optionally from 1 to 3 heteroatoms, optionally wherein the polyaromatic

hydrocarbon is selected from naphthalene, substituted naphthalenes such as di-hydroxynaphthalene, anthracene, tetracene, pentacene, fluorene, acenaphthene, phenanthrene, fluoranthrene, pyrene, chrysene, perylene, coronene, fluorenone, anthraquinone, anthrone and alkyl-substituted derivatives thereof.

The carbon precursors used may be used in pure form, or diluted mixture with an inert carrier gas, such as nitrogen or argon. For instance, the carbon precursor may be used in an amount in the range from 0.1 to 100 vol%, or 20 to 95 vol%, or 50 to 90 vol%, or 60 to 85 vol% based on the total volume of the precursor and the inert carrier gas.

The silicon deposited in the CVI deposition has hydride-terminated silicon surfaces that are highly reactive to oxygen. The process of the invention therefore preferably comprises a passivation step whereby the composite particles can undergo controlled passivation to form a passivated material that is stable in air.

Passivation as described herein may be carried out in the same pressure reactor as step (b). Alternatively, the composite particles formed in step (b) may be removed from the pressure reactor after step (b) and transferred to a post-treatment vessel under inert conditions, followed by passivation in the post-treatment vessel.

Therefore, the process of the invention may further comprise the step of: contacting the composite particles with a passivating agent at conditions that are effective to passivate the composite particles. As defined herein, a passivating agent is a compound or mixture of compounds which is able to react with the surface of the deposited silicon to form a modified surface. The composite particles may be contacted with a passivating agent in the pressure reactor, or may be conveyed to a separate vessel for contacting with a passivating agent. The composite particles may be contacted with a first passivating agent in the pressure reactor, subsequently conveyed to a separate vessel and contacted with a second passivating agent, wherein the first and second passivating agents may be the same or may be different. Preferably the composite particles are at least contacted with a passivating agent in the pressure reactor.

The process of the invention may also comprise the steps of: discontinuing deposition of the silicon to form intermediate composite particles; contacting the intermediate composite particles with a passivating agent at conditions that are effective to passivate the intermediate composite particles to provide passivated intermediate composite particles;

and contacting the passivated intermediate composite particles with the silicon precursor gas at conditions effective to cause deposition of silicon in the pores of the passivated intermediate composite particles to provide composite particles.

- 5 Composite particles that have been contacted with a carbon precursor gas at conditions that are effective to cause deposition of carbon within the pores and/or on the surface of the composite particles may subsequently be contacted with a passivating agent at conditions that are effective to passivate the composite particles.

The passivating agent may be selected from (i) an oxygen containing gas; (ii) ammonia; (iii) a gas comprising ammonia and oxygen; and (iv) phosphine.

- 10 The passivating agent may be an oxygen containing gas. In this case, conditions that are effective to passivate the composite particles may comprise a temperature in the range from 20 to 300 °C, or from 20 to 200 °C, or from 25 to 200 °C, or from 25 to 180 °C, or from 50 °C to 160 °C. Preferably, the temperature is no more than 150 °C. Further, conditions that are effective to passivate the composite particles may comprise a pressure in the range from 1
15 to 600 kPa, or from 10 to 500 kPa, or from 20 to 200 kPa, or from 50 to 150 kPa, or from 80 to 120 kPa, or about 100 kPa. The oxygen containing gas may be air. When the oxygen containing gas is air, the concentration of oxygen in contact with the composite particles during the passivation step may be increased over a period of time, optionally as the composite particles are cooled down to a temperature less than 50 °C.
- 20 The passivating agent may be ammonia or another nitrogen containing molecule. In this case, the passivation layer may comprise a silicon nitride of the formula SiN_x , wherein $0 < x \leq 4/3$. The silicon nitride is preferably amorphous silicon nitride. A nitride layer may be formed by contacting the composite particles with ammonia at a temperature in the range from 200-700 °C, preferably from 400-700 °C, more preferably from 400-600 °C. The
25 temperature may then be increased if necessary into the range of 500 to 1,000 °C to form a nitride surface (e.g. a silicon nitride surface of the formula SiN_x , wherein $x \leq 4/3$). As sub-stoichiometric nitrides (such as SiN_x , wherein $0 < x \leq 4/3$) are conductive, nitride interlayers function as a conductive network that allows for faster charging and discharging of the electroactive material.
- 30 Phosphine may also be used as a passivating agent, as a phosphorus analogue of ammonia.

The passivating agent may comprise ammonia (or another nitrogen containing molecule) and oxygen gas. In this case, the passivation layer may comprise a silicon oxynitride of the formula SiO_xN_y , wherein $0 < x < 2$, $0 < y < 4/3$, and $0 < (2x+3y) \leq 4$. The silicon nitride is preferably amorphous silicon oxynitride. An oxynitride layer may be formed by contacting the composite particles with a passivating agent comprising ammonia (or another nitrogen containing molecule) and oxygen gas.

Other suitable passivating agents include compounds comprising an alkene, alkyne or carbonyl functional group, more preferably a terminal alkene, terminal alkyne, aldehyde or ketone group.

Preferred passivating agents include one or more compounds of the formulae:

- (i) $\text{R}^1\text{-CH=CH-R}^1$;
- (ii) $\text{R}^1\text{-C}\equiv\text{C-R}^1$; and
- (iii) $\text{O=CR}^1\text{R}^1$;

wherein each R^1 independently represents H or an unsubstituted or substituted aliphatic or aromatic hydrocarbyl group having from 1 to 20 carbon atoms, or wherein two R^1 groups form an unsubstituted or substituted ring structure comprising from 3 to 8 carbon atoms in the ring.

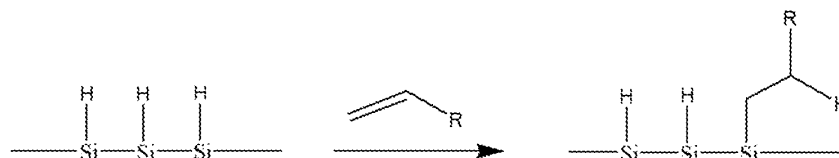
Particularly preferred passivating agents include one or more compounds of the formulae:

- (i) $\text{CH}_2=\text{CH-R}^1$; and
- (ii) $\text{HC}\equiv\text{C-R}^1$;

wherein R^1 is as defined above. Preferably, R^1 is unsubstituted.

Examples of suitable passivating agents include ethylene, propylene, 1-butene, butadiene, 1-pentene, 1,4-pentadiene, 1-hexene, 1-octene, styrene, divinylbenzene, acetylene, phenylacetylene, norbornene, norbornadiene and bicyclo[2.2.2]oct-2-ene. Optionally, mixtures of different passivating agents may also be used.

It is believed that passivating agents comprising an alkene, alkyne or carbonyl group undergo an insertion reaction with M-H groups at the surface of the electroactive material (where M represents an atom of the electroactive material) to form a covalently passivated surface which is resistant to oxidation by air. When silicon is the electroactive material, the passivation reaction between the silicon surface and the passivating agent may be understood as a form of hydrosilylation, as shown schematically below.



Other suitable passivating agents include compounds including an active hydrogen atom bonded to oxygen, nitrogen, sulphur or phosphorus. For example, the passivating agent may be an alcohol, amine, thiol or phosphine. Reaction of the group $-XH$ with hydride groups at the surface of the electroactive material is understood to result in elimination of H_2 and the formation of a direct bond between X and the electroactive material surface.

Suitable passivating agents in this category include compounds of the formula

(iv) $HX-R^2$, and

(v) $HX-C(O)-R^1$,

wherein X represents O, S, NR^1 or PR^1 ; each R^1 is independently as defined above; and R^2 represents an unsubstituted or substituted aliphatic or aromatic hydrocarbyl group having from 1 to 20 carbon atoms, or R^1 and R^2 together form an unsubstituted or substituted ring structure comprising from 3 to 8 carbon atoms in the ring.

Preferably X represents O or NH.

Preferably R^2 represents an optionally substituted aliphatic or aromatic group having from 2 to 10 carbon atoms. Amine groups may also be incorporated into a 4-10 membered aliphatic or aromatic ring structure, as in pyrrolidine, pyrrole, imidazole, piperazine, indole, or purine.

Contacting of the composite particles with the passivating agent may be carried out at a temperature in the range of 25 to 700 °C, preferably at a temperature in the range of from 50 to 500 °C, more preferably from 100 to 300 °C.

A further suitable passivating agent is selected from liquid water and water vapour, preferably wherein the silicon-containing composite particles from step (b) are contacted with the liquid water or water vapour at a temperature in the range from 40 to 400 °C, or from 100 to 350 °C, or from 120 to 300 °C, or from 140 to 280 °C.

The present invention is further described with reference to the following examples.

EXAMPLES

Multiple runs of silicon CVI into porous carbon particles were performed in a pressure reactor with $L_{RV} = 30$ litres and mechanical agitation.

5

The specification of the porous carbon particles was:

Total volume of micropores and mesopores = 0.65 to 0.9 cm³/g

BET surface area = 1600 to 1800 m²/g

10 PD₅₀ pore diameter = 1 to 2 nm

Micropore volume = 0.4 to 0.6 cm³/g

D₅₀ particle diameter = 6 to 8 μm

15

The same reactor volume and agitation, and porous carbon particle specifications were used in the following examples (including comparative).

Example

The following describes an example of the invention using semi-continuous operation:

20

Multiple runs of silicon CVI into porous carbon particles were performed. For each run a 3.3 kg charge of porous carbon particles was provided in the pressure reactor. During the reaction the porous carbon particles were fluidised by mechanical agitation. The reactor was heated to a temperature between 365 and 395 °C and purged with nitrogen before
25 introducing silane (SiH₄) as the silicon precursor gas with a 100 vol% concentration. The silane flow rates used were between 1.1 and 1.7×10^{-7} g_{Si}/m²/min and the reactor was pressurised between 250 and 1200 kPa. The total infiltration time to achieve the target silicon mass of 40-60wt% was between 400 up to 563 minutes. Once the target silicon mass was achieved, the silane flow was stopped and the reactor was depressurized, cooled
30 and purged with nitrogen. The composite particles were chemically stabilised using controlled passivation of silicon in air.

Comparative Example

The following describes a comparative example using a batch-type operation:

- 5 A 4.1 kg charge of porous carbon particles was provided in the pressure reactor. During the reaction the porous carbon particles were fluidised by mechanical agitation. The reactor was then heated to a temperature between 365 and 395 °C and purged with nitrogen before introducing the first dose of silane (SiH_4) as the silicon precursor gas with a 100 vol% concentration. The pressure reactor was sealed after addition of the dose of silane to initiate
- 10 the CVI reaction. The pressure development in the pressure reactor during the reaction was at least between 1810 up to 2030 kPa. After the reaction, byproduct gas was released from the pressure reactor, during which the pressure in the reactor decreased to approximately atmospheric pressure ready for the next silane dose. This dosing cycle was repeated several times to achieve the same target silicon mass as in the example of the
- 15 invention, resulting in infiltration times between 1577 and 3557 minutes. After the target silicon mass was achieved, the silane dosing was stopped and the reactor depressurized, cooled and purged with nitrogen. The composite particles were chemically stabilised using controlled passivation of silicon in air.
- 20 The example according to the invention results in an increase in the process throughput, not only by reducing the production time associated with fluctuations of pressure and repeated additions of silicon precursor gas required to achieve the desired silicon content in the composite particles, but also by reducing the actual infiltration reaction time.

CLAIMS

1. A process for preparing composite particles, the process comprising the steps of:
 - (a) providing a charge of porous particles in a pressure reactor, wherein the charge of porous particles has a total surface area of at least $8.0 \times 10^4 \text{ m}^2$ per litre of reactor volume ($\text{m}^2/\text{L}_{\text{RV}}$);
 - (b) continuously supplying a silicon precursor gas to the pressure reactor while subjecting the porous particles to reaction conditions effective to cause deposition of silicon in the pores of the porous particles, thereby providing composite particles comprising a porous particle framework and silicon within the pores of the porous particle framework, wherein the reaction conditions include agitation of the particles.
2. A process according to claim 1, wherein the charge of porous particles has a total surface area of at least $9.0 \times 10^4 \text{ m}^2/\text{L}_{\text{RV}}$, or at least $1.0 \times 10^5 \text{ m}^2/\text{L}_{\text{RV}}$, or at least $1.1 \times 10^5 \text{ m}^2/\text{L}_{\text{RV}}$, or at least $1.2 \times 10^5 \text{ m}^2/\text{L}_{\text{RV}}$, or at least $1.3 \times 10^5 \text{ m}^2/\text{L}_{\text{RV}}$, or at least $1.4 \times 10^5 \text{ m}^2/\text{L}_{\text{RV}}$, or at least $1.5 \times 10^5 \text{ m}^2/\text{L}_{\text{RV}}$, or at least $1.6 \times 10^5 \text{ m}^2/\text{L}_{\text{RV}}$, or at least $1.8 \times 10^5 \text{ m}^2/\text{L}_{\text{RV}}$, or at least $2.0 \times 10^5 \text{ m}^2/\text{L}_{\text{RV}}$, or at least $2.2 \times 10^5 \text{ m}^2/\text{L}_{\text{RV}}$, or at least $2.5 \times 10^5 \text{ m}^2/\text{L}_{\text{RV}}$.
3. A process according to claim 1 or claim 2, wherein the charge of porous particles has a total surface area of no more than $1.0 \times 10^6 \text{ m}^2/\text{L}_{\text{RV}}$, or no more than $9.0 \times 10^5 \text{ m}^2/\text{L}_{\text{RV}}$, or no more than $8.0 \times 10^5 \text{ m}^2/\text{L}_{\text{RV}}$, or no more than $7.0 \times 10^5 \text{ m}^2/\text{L}_{\text{RV}}$, or no more than $6.0 \times 10^5 \text{ m}^2/\text{L}_{\text{RV}}$, or no more than $5.0 \times 10^5 \text{ m}^2/\text{L}_{\text{RV}}$, or no more than $4.0 \times 10^5 \text{ m}^2/\text{L}_{\text{RV}}$.
4. A process according to any preceding claim, wherein the porous particles comprise micropores and/or mesopores.
5. A process according to claim 4, wherein the porous particles have:
 - (i) a D_{50} particle diameter in the range from 0.5 to 200 μm ;
 - (ii) a total pore volume of micropores and mesopores as measured by gas adsorption in the range from 0.4 to 2.2 cm^3/g ; and
 - (iii) a PD_{50} pore diameter as measured by gas adsorption of no more than 30 nm.
6. A process according to any preceding claim, wherein the flow rate of the silicon precursor gas into the pressure reactor in grams of silicon per m^2 of porous particle surface area per minute in step (b) is at least $3 \times 10^{-7} \text{ g}_{\text{Si}}/\text{m}^2/\text{min}$, or at least $4 \times 10^{-7} \text{ g}_{\text{Si}}/\text{m}^2/\text{min}$, or at least $5 \times 10^{-7} \text{ g}_{\text{Si}}/\text{m}^2/\text{min}$, or at least $6 \times 10^{-7} \text{ g}_{\text{Si}}/\text{m}^2/\text{min}$, or at least $8 \times 10^{-7} \text{ g}_{\text{Si}}/\text{m}^2/\text{min}$, or

at least 1.0×10^{-6} g_{Si}/m²/min, or at least 1.2×10^{-6} g_{Si}/m²/min, or at least 1.5×10^{-6} g_{Si}/m²/min, or at least 2.0×10^{-6} g_{Si}/m²/min.

7. A process according to any preceding claim, wherein the flow rate of the silicon precursor gas into the pressure reactor in grams of silicon per m² porous particle surface area per minute is no more than 5.0×10^{-5} g_{Si}/m²/min, or no more than 2.5×10^{-5} g_{Si}/m²/min, or no more than 2.0×10^{-5} g_{Si}/m²/min, or no more than 1.5×10^{-5} g_{Si}/m²/min, or no more than 1.0×10^{-5} g_{Si}/m²/min, or no more than 8.0×10^{-6} g_{Si}/m²/min, or no more than 6.0×10^{-6} g_{Si}/m²/min, or no more than 5.0×10^{-6} g_{Si}/m²/min, or no more than 4.0×10^{-6} g_{Si}/m²/min, or no more than 3.0×10^{-6} g_{Si}/m²/min.
8. A process according to any preceding claim, wherein the charge of porous particles in step (a) is at least 500 g, or at least 1 kg, or at least 2 kg, or at least 5 kg, or at least 10 kg, or at least 15 kg, or at least 20 kg, or at least 30 kg, or at least 40 kg, or at least 50 kg, or at least 100 kg, or at least 200 kg, or at least 500 kg, or at least 1,000 kg, or at least 5,000 kg, or at least 10,000 kg.
9. A process according to any preceding claim, wherein step (b) comprises mechanically agitating the porous particles, preferably continuously mechanically agitating the porous particles, preferably mechanically fluidising the porous particles.
10. A process according to any preceding claim, wherein the conditions in step (b) include a reaction temperature in the range from 340 to 500 °C, or from 350 to 500 °C, or from 350 to 480 °C, or from 350 to 450 °C, or from 350 to 420 °C, or from 340 to 400 °C, or from 340 to 395 °C, or from 340 to 390 °C, or from 345 to 400 °C, or from 345 to 395 °C, or from 345 to 390 °C, or from 350 to 400 °C, or from 350 to 395 °C, or from 350 to 390 °C, or from 350 to 385 °C, or from 350 to 380 °C, or from 355 to 400 °C, or from 355 to 395 °C, or from 355 to 390 °C, or from 355 to 385 °C, or from 355 to 380 °C, or from 360 to 400 °C, or from 360 to 395 °C, or from 360 to 390 °C, or from 360 to 385 °C, or from 360 to 380 °C, or from 365 to 400 °C, or from 365 to 395 °C, or from 365 to 390 °C, or from 365 to 385 °C, or from 365 to 380 °C, or from 370 to 400 °C, or from 370 to 395 °C, or from 370 to 390 °C, or from 370 to 385 °C, or from 370 to 380 °C.
11. A process according to any preceding claim, wherein the conditions in step (b) include a pressure in the range from 50 to 5,000 kPa, or from 50 to 2,000 kPa, or from 120 to 1,800 kPa, or from 150 to 1,600 kPa, or from 200 to 1,500 kPa, or from 250 to 1,200 kPa,

or from 300 to 1,100 kPa, or from 400 to 1000 kPa, or from 500 to 900 kPa, or from 600 to 800 kPa.

12. A process according to any preceding claim, wherein the partial pressure of the silicon precursor in the pressure reactor during step (b) is at least 20 kPa, or at least 30
5 kPa, or at least 40 kPa, or at least 50 kPa, or at least 60 kPa, or at least 70 kPa, or at least 80 kPa, or at least 90 kPa, or at least 100 kPa, or at least 105 kPa, or at least 110 kPa, or at least 115 kPa, or at least 120 kPa, or at least 150 kPa, or at least 200 kPa, or at least 250 kPa, or at least 300 kPa, or at least 400 kPa, or at least 500 kPa, or at least 600 kPa.

13. A process according to any preceding claim, wherein the partial pressure of the
10 silicon precursor in the pressure reactor during step (b) is no more than 5000 kPa, or no more than 2000 kPa, or no more than 1600 kPa, or no more than 1500 kPa, or no more than 1200 kPa, or no more than 1000 kPa, or no more than 900 kPa, or no more than 800 kPa.

14. A process according to any preceding claim, further comprising continuously or
15 semi-continuously withdrawing an effluent gas from the pressure reactor.

15. A process according to any preceding claim, wherein step (b) comprises adjusting the flow rate of the silicon precursor into the pressure reactor from an initial flow rate to an adjusted flow rate, wherein the adjusted flow rate is less than the initial flow rate, optionally wherein the adjusted flow rate is no more than 90% or no more than 80% or no more than
20 70%, or no more than 60% or no more than 50% of the initial flow rate.

16. A process according to claim 15, wherein the flow rate of the silicon precursor is adjusted after at least 15 %, or at least 20 %, or at least 25 %, or at least 30 %, or at least 35 %, or at least 40 %, or at least 45 %, or at least 50 %, or at least 55 %, or at least 60 %, or at least 65 %, or at least 70 %, or at least 75 %, or at least 80 %, or at least 85 %, or at
25 least 90 % of the target silicon content by mass has been introduced into the reactor in the form of the silicon precursor gas.

17. A process according to any preceding claim, wherein step (b) comprises adjusting the internal pressure of the pressure reactor from an initial pressure to an adjusted pressure, wherein the adjusted pressure is greater than the initial pressure, optionally wherein the
30 adjusted pressure is at least 10%, or at least 20, or at least 30%, or at least 40%, or at least

50%, or at least 60 %, or at least 70 %, or at least 80 %, or at least 90 %, or at least 100 %, or at least 200%, or at least 500%, or at least 1,000% higher than the initial pressure.

18. A process according to claim 17, wherein the internal pressure of the pressure reactor is adjusted after at least 15 %, or at least 20 %, or at least 25 %, or at least 30 %, or at least 35 %, or at least 40 %, or at least 45 %, or at least 50 %, or at least 55 %, or at least 60 %, or at least 65 %, or at least 70 %, or at least 75 %, or at least 80 %, or at least 85 %, or at least 90 % of the target silicon content by mass has been introduced into the reactor in the form of the silicon precursor gas.

19. A process according to any preceding claim, wherein the silicon precursor is selected from silane (SiH_4), disilane (Si_2H_6), trisilane (Si_3H_8), methylsilane, dimethylsilane and chlorosilanes.

20. A process according to any preceding claim, wherein the concentration of the silicon precursor as a proportion of the silicon precursor gas introduced into the reactor is at least 20 vol%, or at least 30 vol%, or at least 40 vol%, or at least 50 vol%, or at least 60 vol%, or at least 70 vol%, or at least 80 vol%, or at least 90 vol%, or at least 95 vol%, or at least 98 vol%, or at least 99 vol%, or at least 99.9 vol%, or at least 99.99 vol%.

21. A process according to any preceding claim, wherein the composite particles formed in step (b) comprise at least 26 wt% silicon, or at least 28 wt% silicon, or at least 30 wt% silicon, or at least 32 wt% silicon, or at least 34 wt% silicon, or at least 36 wt% silicon, or at least 38 wt% silicon, or at least 40 wt% silicon, or at least 42 wt% silicon, or at least 44 wt% silicon.

22. A process according to any preceding claim, wherein the composite particles formed in step (b) comprise no more than 62 wt% silicon, or no more than 60 wt% silicon, or no more than 58 wt% silicon, or no more than 56 wt% silicon, or no more than 54 wt% silicon.

23. A process according to any preceding claim, wherein the process further comprises the step of contacting the composite particles from step (b) with a passivating agent under conditions that are effective to passivate the composite particles.

24. A process according to claim 23, wherein the passivating agent is selected from (i) an oxygen containing gas; (ii) ammonia; (iii) a gas comprising ammonia and oxygen; and (iv) phosphine.

25. A process according to claim 23, wherein the passivating agent is selected from:

(i) $R^1\text{-CH=CH-R}^1$;

(ii) $R^1\text{-C}\equiv\text{C-R}^1$;

(iii) $\text{O=CR}^1\text{R}^1$;

5 (iv) HX-R^2 , and

(v) HX-C(O)-R^1 ,

wherein X represents O, S, NR^1 or PR^1 ; and

wherein each R^1 independently represents H or an unsubstituted or substituted aliphatic or aromatic hydrocarbyl group having from 1 to 20 carbon atoms, or wherein two
10 R^1 groups form an unsubstituted or substituted ring structure comprising from 3 to 8 carbon atoms in the ring;

wherein R^2 represents an unsubstituted or substituted aliphatic or aromatic hydrocarbyl group having from 1 to 20 carbon atoms, or wherein R^1 and R^2 together form an unsubstituted or substituted ring structure comprising from 3 to 8 carbon atoms in the
15 ring.

26. A process according to any preceding claim, further comprising contacting the composite particles from step (b) with a carbon precursor gas at a temperature effective to cause the deposition of carbon into the pores and/or onto the outer surface of the composite particles.

20 27. A process according to any preceding claim, wherein the pressure reactor has an aspect ratio (height/diameter) of at least 0.5, or at least 0.8, or at least 1.