

Process for the Preparation of Composite Particles

INTRODUCTION

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

BACKGROUND TO THE INVENTION

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
10 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
15 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
20 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
25 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).

30 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.

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 particle framework, e.g. a porous carbon material (see WO 2020/095067 and WO 2020/128495). In WO 2022/029422, the applicant has reported a further development of these materials in which the pore size distribution and the deposition of the silicon are both carefully controlled in order to obtain composite materials in which the electroactive material is primarily in the form of very finely divided nanostructures and in which coarser domains of electroactive material are substantially absent. These materials are found to have exceptional reversible capacity retention performance over multiple charge-discharge cycles.

The materials described in WO 2020/095067 and WO 2020/128495 have been synthesized by chemical vapour infiltration (CVI) in various reactor systems, including static bed, fluidized bed and rotary kiln systems.

CVI involves contacting a porous particle framework with a gaseous precursor of the electroactive material under conditions where the gaseous precursor infiltrates the pore structure of the porous particle framework and is thermally decomposed to form the electroactive material. Such processes must be carefully designed in order to obtain the required deposition of the electroactive material into the pore structure of the particle framework. Too high a concentration of the precursor gas can result in rapid and uncontrolled deposition in the outermost pores which then blocks access to much of the available pore volume. As a result, the deposited electroactive material 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 gas means that the reaction time to achieve the necessary silicon loading in the composite particles is relatively long, reducing throughput. Careful temperature control is also necessary. The reaction temperature must be high enough to
5 ensure efficient reaction but not so high that decomposition occurs before the precursor gas can diffuse into the pore network of the particle framework. Temperature deviations within a reactor can also cause inhomogenous reaction rates, resulting in a poor quality product.

The applicant has reported in WO 2023/203352 a method for the production of composite particles in which a continuous supply of a silicon precursor gas is used to obtain high
10 throughput while maintaining controlled and homogenous deposition of silicon into the pore structure of the particle framework.

A key consideration for any industrial process is the efficient utilisation of starting materials. It is therefore desirable in CVI processes as described above for the precursor gas to be fully utilised, such that essentially all of the electroactive material content of the precursor
15 gas is converted into electroactive structures deposited into the porous particle framework. Unreacted precursor gas in effluent gas streams needs to be recovered and recycled adding complexity to the process.

A further consideration for CVI processes as described above is to be able to tailor the CVI conditions to the stage of reaction. The nature of the CVI substrate changes throughout the
20 course of the CVI process from the porous particle starting material, which typically has high porosity, high surface area and contains none of the electroactive material, to a composite particle having relatively much lower pore volume and surface area and a relatively high content of electroactive material. The considerations that drive efficient reaction performance therefore change throughout the course of the CVI process and it would be
25 desirable to be able to adapt the CVI conditions at different stages of the CVI process.

There is therefore a need for improved CVI processes for the manufacture of composite particles of the type described above in which there is improved utilisation of the precursor gas. There is also a need for improved CVI processes in which the CVI reaction conditions can be adapted to different stages of the reaction. It is furthermore a requirement that such
30 CVI processes be operable on a large scale with high throughput while maintaining high utilization of the precursor gas.

SUMMARY OF THE INVENTION

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 reactor;
- 5 (b) contacting the porous particles with a gaseous precursor of an electroactive material in a reactor under conditions of temperature and pressure effective to cause deposition of the electroactive material into the pores of the porous particles to form the composite particles,

wherein step (b) comprises:

- 10 (b1) at least one discontinuous deposition phase during which the charge of porous particles is contacted with a charge of the gaseous precursor and the reactor is sealed during deposition of the electroactive material; and
- (b2) a continuous deposition phase during which the porous particles are contacted with the gaseous precursor in a reactor, wherein the gaseous precursor
- 15 is supplied to the reactor continuously during deposition of the electroactive material.

The invention therefore relates in general terms to a process for preparing a composite particulate material in which an electroactive material is deposited into the pore network of porous particles by a process of chemical vapour infiltration, i.e. by the thermal

20 decomposition of a gaseous precursor of the electroactive material. The composite particles therefore comprise a first component in the form of porous particle framework that is derived from the porous particles provided in step (a), and a second component in the form of a plurality of electroactive material domains that are disposed within the pore structure of the porous particle framework in step (b).

- 25 The process of the invention requires the deposition of the electroactive material in step (b) to be carried out in at least two distinct phases.

In a phase (b1), the gaseous precursor is contacted with the porous particles in a sealed reactor. A fixed charge of the gaseous precursor is added to the reactor and the reactor is then sealed such that the CVI reaction in a phase (b1) occurs without simultaneous addition

30 of additional precursor gas and without removal of by-products.

In phase (b2), the CVI reaction occurs with a continuous flow of the gaseous precursor, such that the precursor gas is supplied to the reactor vessel simultaneously with the CVI reaction in progress.

The process of the invention was conceived in response to the observation a CVI process involving continuous supply of the precursor gas under steady state conditions does not involve a uniform rate of consumption of the precursor gas. Instead, it is found that the rate of consumption of the precursor gas is low at the outset of deposition then rapidly increases to a maximum before decreasing again as the pore volume of the porous particles is filled. The slow rate of consumption of the precursor gas at the outset of deposition is believed to be due to a slow rate of seeding of the electroactive material onto the internal pore surfaces of the porous particles. The slow rate of consumption of the precursor gas at the end of deposition is thought to be a consequence of the reduction of the available surface area for deposition as the pore volume of the porous particles becomes filled with the electroactive material.

A process in which the entire deposition of the electroactive material is carried out using continuous supply of the precursor gas under steady state conditions therefore results in poor utilisation of the precursor gas at the start and the end of the process. Meanwhile, if the entire deposition of the electroactive materials is carried out using a fixed charge of the precursor gas in a sealed reactor, high utilization of the precursor gas can be achieved, but the overall process is slow and inefficient, requiring multiple charges of the precursor gas and usually temperature cycling of the reactor.

The invention responds to this problem by providing a process in which part of the deposition is carried out in phase (b1) using a fixed charge of the precursor gas in a sealed reactor such that the precursor gas can be fully consumed. The remainder of the deposition is carried out using a continuous supply of the precursor gas in phase (b2). In this way, the process achieves the benefits of using a fixed charge of precursor gas to initiate and terminate the deposition process, and the efficiencies of a continuous supply of the precursor gas for the bulk of the deposition.

In step (a), the reactor is charged with porous particles. As set out above, the porous particles provide a substrate for the deposition of the electroactive material. Since the majority of the surface area of the porous particles is in the internal pore spaces, deposition

of the electroactive material into the pores is kinetically favoured and therefore the pore dimensions influence the dimensions of the deposited electroactive material domains.

The porous particles may be characterized by their particle size, pore volume, pore size distribution and chemical composition. Suitable porous particles may have:

- 5 (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 nitrogen 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.

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 "D₅₀" and "D₅₀ 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 "D₁₀" and "D₁₀ 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 "D₉₀" and "D₉₀ 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 13320:2020. 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 SPANTM-40 (sorbitan monopalmitate). The particle refractive index is taken to be 2.68 for porous particles and
5 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 D₅₀ particle diameter in the range from 0.5 to 200 µm.

Preferably, the D₅₀ particle diameter of the porous particles is at least 1 µm, or at least
10 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.

Preferably, the D₅₀ particle diameter of the porous particles is no more than 100 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
15 12 µm, or no more than 10 µm, or no more than 8 µm.

For instance, the porous particles may have a D₅₀ particle diameter in the range from 0.5 to 50 µm, or from 0.5 to 30 µm, or from 1 to 25 µm, or from 1.5 to 25 µm, or from 1.5 to 20 µm, or from 2 to 20 µm, or from 2 to 18 µm, or from 2.5 to 18 µm, or from 2.5 to 15 µm, from 3 to 15 µm, or from 3.5 to 15 µm, or from 4 to 15 µm, or from 4 to 12 µm, or from 4.5 to 12 µm,
20 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 D₁₀ particle diameter of the porous particles is preferably at least 0.2 µm, or at least
25 0.5 µm, or at least 0.8 µm, or at least 1 µm, or at least 1.5 µm, or at least 2 µm. By maintaining the D₁₀ particle diameter at 0.2 µm or more, the potential for undesirable agglomeration of sub-micron sized particles is reduced, and improved dispersibility of the composite particles formed.

The D₉₀ particle diameter of the porous particles is preferably no more than 250 µm, or no
30 more than 200 µm, or no more than 150 µm, or no more than 100 µm, or no more than

80 µm, or no more than 60 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 15 µm.

The porous particles preferably have a narrow size distribution span. For instance, the particle size distribution span (defined as $(D_{90}-D_{10})/D_{50}$) is preferably 5 or less, more preferably 4 or less, more preferably 3 or less, more preferably 2 or less, and most preferably 1.5 or less. By maintaining a narrow size distribution span, efficient packing of the particles in continuous reactors is more readily achievable.

The invention may also be used with porous particles in which the plurality of particles have a positive skew in the volume-based particle diameter distribution. Preferably, the D_{50} diameter is less than the volume-based mean particle diameter. Preferably, the skew of the porous particle diameter distribution (as measured by a Malvern MastersizerTM 3000 analyzer) is no more than 4, or no more than 3, or no more than 2, or no more than 1.5. Preferably, the skew is at least 0.2, or at least 0.3, or at least 0.4. The particle diameter distribution of the porous particles may be monomodal, bimodal or multimodal.

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.

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:

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

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 comprise a three-dimensionally interconnected open pore network preferably 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 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 material in step (a) of the claimed process, i.e. prior to deposition of the electroactive material into the pore volume in step (b).

The porous particles may comprise a total volume of micropores and mesopores (i.e. the total pore volume in the range from 0 to 50 nm) in the range from 0.4 to 2.2 cm³/g. Typically, the porous particles include both micropores and mesopores. However, it is not 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. The use of high porosity conductive particles may be advantageous since it allows a larger amount of electroactive material 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 volume accommodating a larger amount of electroactive material. 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, or no more than 1.

For example, the total volume of micropores and mesopores in the porous particles may be
5 in the range from 0.4 to 2.0 cm³/g, or from 0.45 to 1.8 cm³/g, or from 0.5 to 1.6 cm³/g, or from 0.55 to 1.4 cm³/g, or from 0.6 to 1.3 cm³/g, or from 0.65 to 1.2 cm³/g, or from 0.7 to 1.1 cm³/g, or from 0.8 to 1.0 cm³/g.

The PD₅₀ pore diameter of the porous particles is preferably no more than 15 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
10 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 general term "PD_n pore diameter" as used herein refers to the volume-based nth percentile pore diameter, based on the total volume of micropores and mesopores (i.e. the pore diameter below which n% of the total micropore and mesopore volume is found).
15 Therefore, in accordance with the invention, the volume based median pore diameter (PD₅₀) is preferably less than 15 nm.

The volume of larger mesopores in the porous particles is preferably limited such that the PD₉₀ pore diameter is no more than 30 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
20 nm, or no more than 5 nm.

Optionally, the porous particles have PD₅₀ no more than 15 nm and PD₉₀ no more than 30 nm; or PD₅₀ from 1 to 5 nm and PD₉₀ from 3 to 20 nm; or PD₅₀ from 1 to 4 nm and PD₉₀ from 3 to 15 nm; or PD₅₀ from 1 to 3 nm and PD₉₀ from 3 to 12 nm; or PD₅₀ from 1 to 3 nm and PD₉₀ from 3 to 10 nm; or PD₅₀ from 1 to 2.5 nm and PD₉₀ from 3 to 10 nm; or PD₅₀ from 1
25 to 2 nm and PD₉₀ from 3 to 8 nm; or PD₅₀ from 1 to 2 nm and PD₉₀ from 3 to 6 nm; or PD₅₀ from 1 to 2 nm and PD₉₀ from 3 to 6 nm.

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

The volumetric ratio of micropores to mesopores in the porous particles may range in
30 principle from 100:0 to 0:100, or from 90:10 to 5:95, or from 90:10 to 10:90, or from 90:10 to 20:80, or from 90:10 to 35:65, or from 90:10 to 40:60. Preferably, the volumetric ratio of

micropores to mesopores is from 90:10 to 55:45, or from 90:10 to 60:40, or from 85:15 to 65:35.

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 pore size relative to the cumulative total internal pore volume of the porous particles. A
5 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 electroactive material.

The total volume of micropores and mesopores and the pore size distribution of micropores
10 and mesopores are determined using nitrogen gas adsorption at 77 K down to a relative pressure p/p_0 of 10^{-7} using quenched solid density functional theory (QSDFT) in accordance with standard methodology as set out in ISO 15901-2 and ISO 15901-3. 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
15 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
20 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.

Nitrogen gas adsorption is effective for the measurement of pore volume and pore size
25 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). PD_{50} are likewise determined relative to the total volume of micropores and mesopores only.

30 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 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
5 into the pore network, but the advantages of the invention are obtained substantially by accommodating electroactive material in micropores and smaller mesopores.

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
10 assumed for the purposes of the invention to be inter-particle porosity and is also disregarded.

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
15 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/cm³ at room temperature. A number of high precision mercury porosimetry instruments are
20 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.

25 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
30 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 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 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, 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 assessed by monitoring the ratio in peak intensity of the D-band to the G-band (ID/IG).

As used herein, the term “soft carbon” also refers to a disordered carbon matrix in which 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 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.

5 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.

10 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.

15 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. 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. 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. 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.

Preferably the porous particles have:

- 25 (i) a total pore volume of micropores and mesopores as measured by nitrogen gas adsorption in the range from 0.4 to 1.8 cm³/g;
- (ii) a PD₅₀ pore diameter of no more than 10 nm, and preferably a PD₉₀ pore diameter of no more than 20 nm; and
- (iii) a D₅₀ particle diameter in the range from 1 to 20 μm.

30 More preferably the porous particles have:

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(i) a total pore volume of micropores and mesopores as measured by nitrogen gas adsorption in the range from 0.5 to 1.6 cm³/g;

(ii) a PD₅₀ pore diameter of no more than 8 nm, and preferably a PD₉₀ pore diameter of no more than 15 nm; and

5 (iii) a D₅₀ particle diameter in the range from 1 to 18 μm.

More preferably the porous particles have:

(i) a total pore volume of micropores and mesopores as measured by nitrogen gas adsorption in the range from 0.6 to 1.5 cm³/g;

10 (ii) a PD₅₀ pore diameter of no more than 6 nm, and preferably a PD₉₀ pore diameter of no more than 12 nm; and

(iii) a D₅₀ particle diameter in the range from 1.5 to 15 μm.

More preferably the porous particles have:

(i) a total pore volume of micropores and mesopores as measured by nitrogen gas adsorption in the range from 0.65 to 1.4 cm³/g;

15 (ii) a PD₅₀ pore diameter of no more than 2.5 nm, and preferably a PD₉₀ pore diameter of no more than 10 nm; and

(iii) a D₅₀ particle diameter in the range from 1.5 to 12 μm.

More preferably the porous particles have:

20 (i) a total pore volume of micropores and mesopores as measured by nitrogen gas adsorption in the range from 0.7 to 1.3 cm³/g;

(ii) a PD₅₀ pore diameter of no more than 4 nm, and preferably a PD₉₀ pore diameter of no more than 8 nm; and

(iii) a D₅₀ particle diameter in the range from 2 to 10 μm.

More preferably the porous particles have:

25 (i) a total pore volume of micropores and mesopores as measured by nitrogen gas adsorption in the range from 0.75 to 1.2 cm³/g;

(ii) a PD₅₀ pore diameter of no more than 3 nm, and preferably a PD₉₀ pore diameter of no more than 6 nm;

(iii) a D₅₀ particle diameter in the range from 2 to 10 μm.

30 More preferably the porous particles have:

(i) a total pore volume of micropores and mesopores as measured by nitrogen gas adsorption in the range from 0.8 to 1.2 cm³/g;

(ii) a PD₅₀ pore diameter of no more than 2 nm, and preferably a PD₉₀ pore diameter of no more than 5 nm;

5 (iii) a D₅₀ particle diameter in the range from 2.5 to 8 µm.

In order to achieve efficient spatial efficiency of the reactor, the charge of the porous particles in step (a) preferably has a mass of at least 20 g per litre of reactor volume (g/L_{RV}), or at least 50 g/L_{RV}, or at least 80 g/L_{RV}, or at least 100 g/L_{RV}, or at least 150 g/L_{RV}, or at least 200 g/L_{RV}, or at least 250 g/L_{RV}.

10 Phase (b1) represents a phase of the process in which the CVI reaction is carried out in a batch mode for both the porous particles and the gaseous precursor of the electroactive material. The CVI reaction during phase (b1) takes place in a sealed reactor without addition of further gaseous precursor while the reaction is in progress.

The use of a batch charge of the gaseous precursor is associated with several advantages.

15 In particular, the gaseous precursor can diffuse throughout the entire volume of the reactor and therefore the local concentration of the gaseous precursor is not affected by non-homogenous flow patterns of a flowing gaseous precursor. As a result, the CVI reaction can occur homogeneously throughout the entire reactor and throughout the entire mass of porous particles. As a result, the composite material formed in phase (b1) will have
20 consistent properties throughout the composition. As a result, phase (b1) is effective to achieve highly homogeneous seeding of the electroactive material onto the pore surfaces of the porous particles at the outset of the CVI process in step (b) alongside complete consumption of the gaseous precursor. Phase (b1) is also effective to achieve highly controlled deposition toward the end of the CVI, again with complete consumption of the
25 gaseous precursor.

The use of a batch charge of the gaseous precursor in a sealed reactor also has the advantage that the CVI reaction can be carried out until complete conversion of the gaseous precursor is achieved. In circumstances where the rate of conversion is low (e.g. at the beginning or the end of deposition), the use of a continuous feedstream of the gaseous
30 precursor and a continuous effluent stream of gaseous by-products can result in a significant amount of the gaseous precursor passing through the reactor without reacting.

This problem is avoided by the use of a batch charge of the gaseous precursor in a sealed reactor.

Phase (b1) may be the first phase of step (b). Therefore, the CVI process in step (b) may commence with a phase (b1) to seed the electroactive material onto the pore surfaces of the porous particles followed by subsequent deposition of the electroactive material in phase (b2). Optionally, phase (b1) may be repeated one or more times prior to step (b2).

In the case that phase (b1) is the first phase of step (b), the total amount of the electroactive material deposited in the phase (b1) [or in the two or more phases (b1) if phase (b1) is repeated prior to phase (b2)] may be up to 10 wt% of the total electroactive material deposited in step (b). For example, the total amount of the electroactive material deposited in the phase(s) (b1) prior to phase (b2) may be up to 8 wt%, or up to 6 wt% of the total electroactive material deposited in step (b).

Although it is possible in principle to deposit more than 10 wt% of the total electroactive material in the initial phase(s) (b1), this is time-consuming and reduces the efficiency of the process since deposition of the bulk of the electroactive material after initial seeding in phase (b1) is most efficiently carried out using a continuous supply of the precursor gas in phase (b2).

In the case that phase (b1) is the first phase of step (b), the total amount of the electroactive material deposited in the phase (b1) [or in the two or more phases (b1) if phase (b1) is repeated prior to phase (b2)] is preferably at least 0.5 wt% of the total electroactive material deposited in step (b). For example, the total amount of the electroactive material deposited in the phase(s) (b1) prior to phase (b2) may be at least 1 wt%, or at least 2 wt%, or at least 3 wt%, or at least 4 wt%, or at least 5 wt% of the total electroactive material deposited in step (b). It has been found that amounts within these ranges are effective for efficient seeding of the electroactive material prior to phase (b2).

In the case that phase (b1) is the first phase of step (b), the total amount of the electroactive material deposited in the phase (b1) [or in the two or more phases (b1) if phase (b1) is repeated prior to phase (b2)] is preferably at least 0.005 g per g of the porous carbon framework (g/g). For example, the total amount of the electroactive material deposited in the phase(s) (b1) prior to phase (b2) may be at least 0.01 g/g, or at least 0.015 g/g, or at least 0.02 g/g, or at least 0.03 g/g, or at least 0.04 g/g, or at least 0.05 g/g.

Phase (b1) may be the final phase of step (b). Therefore, the CVI process in step (b) concludes with a phase (b1) to ensure high consumption of the gaseous precursor and controlled deposition in the final phase of the CVI process following phase (b2). Optionally, phase (b1) may be repeated one or more times after step (b2).

- 5 In the case that phase (b1) is the final phase of step (b), the total amount of the electroactive material deposited in the phase (b1) [or in the two or more phases (b1) if phase (b1) is repeated after phase (b2)] may be up to 10 wt% of the total electroactive material deposited in step (b). For example, the total amount of the electroactive material deposited in the phase(s) (b1) after phase (b2) may be up to 8 wt%, or up to 6 wt% of the total electroactive material deposited in step (b).
- 10

- In the case that phase (b1) is the final phase of step (b), the total amount of the electroactive material deposited in the phase (b1) [or in the two or more phases (b1) if phase (b1) is repeated after phase (b2)] is preferably at least 0.5 wt% of the total electroactive material deposited in step (b). For example, the total amount of the electroactive material deposited
- 15 in the phase(s) (b1) after phase (b2) may be at least 1 wt%, or at least 2 wt%, or at least 3 wt%, or at least 4 wt%, or at least 5 wt% of the total electroactive material deposited in step (b).

- In the case that phase (b1) is the final phase of step (b), the total amount of the electroactive material deposited in the phase (b1) [or in the two or more phases (b1) if phase (b1) is repeated after phase (b2)] is preferably at least 0.005 g per g of the porous carbon framework (g/g). For example, the total amount of the electroactive material deposited in the phase(s) (b1) after phase (b2) may be at least 0.01 g/g, or at least 0.015 g/g, or at least 0.02 g/g, or at least 0.03 g/g, or at least 0.04 g/g, or at least 0.05 g/g.
- 20

- Optionally, step (b) may comprise a phase (b1) as both the first and the last phase. In this case, phase (b1) may also optionally be repeated one or more times prior to and/or after phase (b2). For example, step (b) may comprise three phases in which the first phase is a discontinuous phase (b1), the second phase is a continuous phase (b2) and the third phase is a discontinuous phase (b1).
- 25

- The electroactive material deposited in step (b) may be selected from silicon, tin, aluminium and germanium and mixtures thereof. Optionally, different electroactive materials may be deposited in phase (b1) and phase (b2). However, most preferably, the same electroactive material is deposited in phase (b1) and phase (b2).
- 30

Preferably, the electroactive material deposited in step (b) is silicon and therefore the preferred precursor gas is a silicon precursor gas. Suitable silicon precursors include silane (SiH_4), disilane (Si_2H_6), trisilane (Si_3H_8), tetrasilane (Si_4H_{10}), methylsilane (CH_3SiH_3), dimethylsilane ($(\text{CH}_3)_2\text{SiH}_2$), trimethylsilane ($(\text{CH}_3)_3\text{SiH}$), tetramethylsilane ($(\text{CH}_3)_4\text{Si}$), or
 5 chlorosilanes such as trichlorosilane (HSiCl_3) or dichlorosilane (H_2SiCl_2) or chlorosilane (H_3SiCl), or methylchlorosilanes such as methyltrichlorosilane (CH_3SiCl_3) or dimethyldichlorosilane ($(\text{CH}_3)_2\text{SiCl}_2$). Preferably the silicon precursor is selected from silane (SiH_4), disilane (Si_2H_6), trisilane (Si_3H_8), tetrasilane (Si_4H_{10}). A particularly preferred silicon precursor is silane (SiH_4).

10 Suitable germanium precursors include germane (GeH_4), hexamethyldigeranium ($(\text{CH}_3)_3\text{GeGe}(\text{CH}_3)_3$), tetramethylgermanium ($(\text{CH}_3)_4\text{Ge}$), tributylgermanium hydride ($[(\text{CH}_3(\text{CH}_2)_3)_3\text{GeH}]$), triethylgermanium hydride ($(\text{C}_2\text{H}_5)_3\text{GeH}$), and triphenylgermanium hydride ($(\text{C}_6\text{H}_5)_3\text{GeH}$). A preferred germanium precursor is germane.

Suitable tin precursors include bis[bis(trimethylsilyl)amino]tin(II) ($[(\text{CH}_3)_3\text{Si}]_2\text{N}_2\text{Sn}$),
 15 tetraallyltin ($(\text{H}_2\text{C}=\text{CHCH}_2)_4\text{Sn}$), tetrakis(diethylamido)tin(IV) ($[(\text{C}_2\text{H}_5)_2\text{N}]_4\text{Sn}$), tetrakis(dimethylamido)tin(IV) ($[(\text{CH}_3)_2\text{N}]_4\text{Sn}$), tetramethyltin ($\text{Sn}(\text{CH}_3)_4$), tetravinyltin ($\text{Sn}(\text{CH}=\text{CH}_2)_4$), tin(II) acetylacetonate ($\text{C}_{10}\text{H}_{14}\text{O}_4\text{Sn}$), trimethyl(phenylethynyl)tin ($\text{C}_6\text{H}_5\text{C}\equiv\text{CSn}(\text{CH}_3)_3$), and trimethyl(phenyl)tin ($\text{C}_6\text{H}_5\text{Sn}(\text{CH}_3)_3$). A preferred tin precursor is tetramethyltin.

20 Suitable aluminium precursors include aluminium tris(2,2,6,6-tetramethyl-3,5-heptanedionate) ($\text{Al}(\text{OCC}(\text{CH}_3)_3\text{CHCOC}(\text{CH}_3)_3)_3$), trimethylaluminium ($(\text{CH}_3)_3\text{Al}$), and tris(dimethylamido)aluminium(III) ($\text{Al}(\text{N}(\text{CH}_3)_2)_3$). A preferred aluminium precursor is trimethylaluminium.

Optionally, the primary electroactive precursor gas may be mixed with a secondary
 25 electroactive precursor gas dosed concomitantly. In addition to the precursor gases already named secondary precursor gases could also include dopant precursor gases. Preferred dopants include acceptor or p-type dopants such as boron, gallium, indium. Suitable precursor gases for such dopants include; diborane, triethyl gallium, indium acetylacetonate. Preferred donors or n-type dopants include phosphorus, nitrogen, arsenic,
 30 antimony, bismuth. Suitable precursors for such n-type dopants include; phosphine, ammonia, arsenic trihydride, antimony n-butoxide, bismuth β -diketonates.

Preferably, the same precursor gas is used in phase (b1) and phase (b2). More preferably, the precursor gas used in phase (b1) and phase (b2) is silane (SiH_4).

The charge of precursor gas used in phase (b1) preferably comprises at least 0.5 g/L_{RV} of the electroactive material, at least 1 g/L_{RV} the electroactive material, at least 2 g/L_{RV} the electroactive material, at least 3 g/L_{RV} the electroactive material, at least 4 g/L_{RV} the electroactive material, or at least 5 g/L_{RV} of the electroactive material, or at least 10 g/L_{RV} of the electroactive material, or at least 15 g/L_{RV} of the electroactive material, or at least 20 g/L_{RV} of the electroactive material, or at least 40 g/L_{RV} of the electroactive material, or at least 60 g/L_{RV} of the electroactive material, or at least 80 g/L_{RV} of the electroactive material, or at least 100 g/L_{RV} of the electroactive material.

More preferably, the electroactive material is silicon and the charge of silicon precursor gas used in phase (b1) preferably comprises at least 0.5 g/L_{RV} of silicon, at least 1 g/L_{RV} silicon, at least 2 g/L_{RV} silicon, at least 3 g/L_{RV} silicon, at least 4 g/L_{RV} silicon, or at least 5 g/L_{RV} of silicon, or at least 10 g/L_{RV} of silicon, or at least 15 g/L_{RV} of silicon, or at least 20 g/L_{RV} of silicon, or at least 40 g/L_{RV} of silicon, or at least 60 g/L_{RV} of silicon, or at least 80 g/L_{RV} of silicon, or at least 100 g/L_{RV} of silicon.

The charge of the gaseous precursor in phase (b1) may be in admixture with an inert gas, for example, nitrogen or argon. Preferably, the admixture 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 gaseous precursor, wherein these values refer to the composition of the gas phase in the reactor prior to any reaction.

In the case that the silicon precursor gas is a chlorosilane, the charge to the reactor in phase (b1) also includes hydrogen gas, preferably in at least a 1:1 atomic ratio of hydrogen to chlorine.

Since the gaseous precursor is essentially fully consumed in phase (b1), the mass ratio of the porous particles supplied to the reactor in step (a) to the gaseous precursor defines the mass ratio of the porous particles to the deposited electroactive material.

The charge of precursor gas in phase (b1) preferably comprises at least 2 g the electroactive material per kg of the porous particles, or at least 3 g the electroactive material per kg of the porous particles, or at least 5 g the electroactive material per kg of the porous particles,

or at least 10 g the electroactive material per kg of the porous particles, or at least 20 g the electroactive material per kg of the porous particles, or at least 30 g the electroactive material per kg of the porous particles, or at least 40 g the electroactive material per kg of the porous particles, or at least 50 g the electroactive material per kg of the porous particles.

- 5 More preferably, the electroactive material is silicon and the charge of silicon precursor gas in phase (b1) preferably comprises at least 2 g silicon per kg of the porous particles, or at least 3 g silicon per kg of the porous particles, or at least 5 g silicon per kg of the porous particles, or at least 10 g silicon per kg of the porous particles, or at least 20 g silicon per kg of the porous particles, or at least 30 g silicon per kg of the porous particles, or at least 40 g silicon per kg of the porous particles, or at least 50 g silicon per kg of the porous particles.
- 10

Phase (b1) preferably comprises evacuation of the reactor prior to addition of the charge of the gaseous precursor. Alternatively, phase (b1) may comprise flushing of the reactor with an inert gas prior to charging the reactor with the gaseous precursor.

- The temperature in phase (b1) is in the range from 320 to 500 °C, or from 320 to 450°C, or from 340 to 450°C, or from 350 to 420 °C, or from 360 to 340 °C, or from 365 to 395 °C, or from 370 to 390 °C. In general, lower temperatures are preferred since the reaction is not limited by mass transfer.
- 15

- Optionally, the charge of the gaseous precursor in phase (b1) is added to the reactor while the reactor is at a temperature below the decomposition temperature of the gaseous precursor. The reactor is sealed and then subsequently heated to the target reaction temperature. In the case that a phase (b1) is carried out after a phase (b2), step (b) may optionally comprise cooling the reactor after phase (b2) to a below the decomposition temperature of the gaseous precursor. The reactor is then charged with the gaseous precursor and the reactor is heated to the required reaction temperature for phase (b1).
- 20

- 25 The maximum pressure in phase (b1) is an autogenous pressure that depends on the respective charges of the porous particles and the gaseous precursor and the internal volume of the reactor. Depending on the stoichiometry of the reaction, the thermal decomposition of the gaseous precursor may result in an increase in pressure. For example, the deposition of silicon from silane gas (SiH_4) results in the elimination of two moles of hydrogen gas per mole of silane gas precursor. As a result, the partial pressure of hydrogen at completion of the reaction is higher than the partial pressure of the unreacted
- 30

silane. Accordingly, the reactor is preferably a pressure reactor that is rated to withstand the pressures that result in phase (b1).

In general, the maximum (autogenous) pressure in phase (b1) is at least 100 kPa, or at least 110 kPa, or at least 120 kPa, or at least 150 kPa, or at least 200 kPa, or at least 300 kPa, or at least 500 kPa, or at least 600 kPa, or at least 700 kPa, or at least 800 kPa, or at least 900 kPa, or at least 1,000 kPa, or at least 1,500 kPa, or at least 2,000 kPa, or at least 2,500 kPa, or at least 3,000 kPa, or at least 4,000 kPa, or at least 5,000 kPa. Step (b1) may optionally be carried out above the critical pressure of the silicon precursor.

Optionally, the maximum pressure in phase (b1) may be no more than 15,000 kPa, or no more than 10,000 kPa, or no more than 8,000 kPa, or no more than 5,000 kPa, or no more than 4,000 kPa, or no more than 2,500 kPa, or no more than 2,000 kPa, or no more than 1,500 kPa, or no more than 1,200 kPa.

All pressure values disclosed herein are absolute pressures unless specified otherwise.

The reactor preferably contains essentially no oxygen (or oxidizing gases) during phase (b1). As defined herein, an oxidizing gas is a gas that is capable of oxidizing the deposited electroactive material under the conditions of the CVI reaction. The main oxidizing gas of concern in practice is atmospheric oxygen. Oxygen can be sufficiently eliminated from the reactor by evacuating the reactor volume and flushing with an inert gas in accordance with standard procedures for reactions carried out oxygen-free atmospheres.

Phase (b2) represents a phase of the process in which the CVI reaction is carried out in a batch mode for the porous particles and in continuous mode for the gaseous precursor of the electroactive material. This means that supply of the gaseous precursor to the reactor takes place simultaneously with the reaction in progress and continuously throughout phase (b2).

In principle, continuous operation does not exclude the possibility of deviations in the rate of flow of gaseous precursor to or effluent gas from the reactor. For example, the flow rate of the gaseous precursor gas into the reactor may be adjusted throughout phase (b2) to account for changes in reaction rate. Alternatively, the gaseous precursor gas may be introduced into the reactor at a constant pressure.

Withdrawal of effluent gases is preferably continuous, such that both the supply of the gaseous precursor and the withdrawal of effluent gas from the reactor occur continuously

and simultaneously with the reaction in progress. However, it is not excluded that the effluent gases may be withdrawn semi-continuously, defined here as alternatingly opening and closing an effluent gas valve during phase (b2). The effluent gas valve may, for example, be a pressure release valve that opens periodically as the production of by-product gases increases the internal pressure of the reactor above a predetermined threshold value.

Operation of the CVI process in phase (b2) allows for continuous replenishment of the gaseous precursor as it is consumed. Since the total volume of the gaseous precursor that can be supplied in phase (b2) is much greater than in phase (b1), phase (b2) allows for a majority of the electroactive material to be deposited under conditions of high throughput.

Operating the reactor under these conditions also means that the CVI deposition proceeds under conditions where fresh gaseous precursor is added before byproducts are removed fully from the system. Thus, as the gaseous precursor is continuously added to the reactor it mixes with byproducts, resulting in a consistent concentration of the gaseous precursor.

In the case that phase (b2) follows phase (b1), phase (b2) may be initiated by activating the supply of the precursor gas to the reactor and by evacuating effluent gases from the reactor.

In the case that the gaseous precursor is a silicon precursor gas, the flow rate of the silicon precursor gas into the reactor in phase (b2) in grams of silicon (g_{Si}) per minute per kg of the porous particles (kg_{PP}) is from 0.2 to 25 $g_{Si} \cdot min^{-1} \cdot kg_{PP}^{-1}$, or from 0.5 to 20 $g_{Si} \cdot min^{-1} \cdot kg_{PP}^{-1}$, or from 1 to 15 $g_{Si} \cdot min^{-1} \cdot kg_{PP}^{-1}$, or from 1 to 14 $g_{Si} \cdot min^{-1} \cdot kg_{PP}^{-1}$, or from 1 to 13 $g_{Si} \cdot min^{-1} \cdot kg_{PP}^{-1}$, or from 1 to 12 $g_{Si} \cdot min^{-1} \cdot kg_{PP}^{-1}$, or from 2 to 12 $g_{Si} \cdot min^{-1} \cdot kg_{PP}^{-1}$.

The space time of the gaseous precursor in contact with the porous particles in phase (b2) may be maintained in the range from 0.2 to 60 min, or from 0.5 to 60 min, or from 1 to 60 min, or from 2 to 45 min, or from 3 to 30 min, or from 4 to 25 min, or from 5 to 20 min. These space times are considerably longer than the space time of gaseous precursor in fluidised bed reactor processes, because in such processes the gaseous precursor must be supplied at a sufficient velocity to fluidise the porous particles. Increasing the space time of the gaseous precursor in contact with the porous particles increases the conversion rate of gaseous precursor.

The space time of the gaseous precursor in the reactor is calculated as the reactor volume in litres divided by the flow rate of gaseous precursor (total gas including gaseous precursor and any diluent gases) into the reactor in L/min at process conditions.

The space velocity of the gaseous precursor, based on the reactor volume, during phase (b2) may be at least 0.02 min^{-1} , or at least 0.025 min^{-1} , or at least 0.03 min^{-1} , or at least 0.035 min^{-1} , or at least 0.04 min^{-1} , or at least 0.045 min^{-1} , or at least 0.05 min^{-1} , or at least 0.06 min^{-1} , or at least 0.07 min^{-1} , or at least 0.08 min^{-1} , or at least 0.09 min^{-1} , or at least 0.1 min^{-1} , or at least 0.15 min^{-1} , or at least 0.2 min^{-1} , or at least 0.25 min^{-1} , or at least 0.3 min^{-1} , or at least 0.35 min^{-1} , or at least 0.4 min^{-1} , or at least 0.5 min^{-1} , or at least 0.7 min^{-1} , or at least 1 min^{-1} , or at least 1.5 min^{-1} .

The space velocity of the gaseous precursor, based on the reactor volume, during phase (b2) may be no more than 3 min^{-1} , or no more than 2 min^{-1} , or no more than 1.5 min^{-1} , or no more than 1 min^{-1} , or no more than 0.8 min^{-1} , or no more than 0.75 min^{-1} , or no more than 0.7 min^{-1} , or no more than 0.65 min^{-1} , or no more than 0.6 min^{-1} , or no more than 0.55 min^{-1} , or no more than 0.5 min^{-1} . These space velocities are considerably lower than the space velocity of gaseous precursor in fluidised bed reactor processes.

The space velocity of the gaseous precursor based on the reactor volume is calculated as the flow rate of gaseous precursor into the reactor in l/min at process conditions divided by the reactor volume in litres. If the gaseous precursor is used in dilution, then space velocity of the gaseous precursor based on the reactor volume is calculated as [the flow rate of gaseous precursor (total gas including gaseous precursor and any diluting gases) into the reactor in L/min at process conditions, divided by the reactor volume in litres] multiplied by the volume fraction (vol%) of the gaseous precursor in the gaseous precursor being introduced into the reactor.

It is preferred that the conditions in phase (b2) include a combination of controlled space time of the gaseous precursor in contact with the porous particles and space velocity of the gaseous precursor based on the reactor volume. This combination defines a set of conditions in which the time that the gaseous precursor is in contact with the porous particles is increased (e.g., compared to fluidised bed reactors), thus increasing the conversion rate of gaseous precursor.

The space time of the gaseous precursor in contact with the porous particles in phase (b2) may be maintained in the range from 1 to 60 min and the space velocity of the gaseous precursor, based on the reactor volume, during phase (b2) may be at least 0.02 min^{-1} .

- 5 The space time of the gaseous precursor in contact with the porous particles in phase (b2) may be maintained in the range from 2 to 45 min and the space velocity of the gaseous precursor, based on the reactor volume, during phase (b2) may be at least 0.025 min^{-1} .

The space time of the gaseous precursor in contact with the porous particles in phase (b2) may be maintained in the range from 3 to 30 min and the space velocity of the gaseous precursor, based on the reactor volume, during phase (b2) may be at least 0.03 min^{-1} .

- 10 The space time of the gaseous precursor in contact with the porous particles in phase (b2) may be maintained in the range from 4 to 25 min and the space velocity of the gaseous precursor, based on the reactor volume, during phase (b2) may be at least 0.035 min^{-1} .

- 15 The space time of the gaseous precursor in contact with the porous particles in phase (b2) may be maintained in the range from 5 to 20 min and the space velocity of the gaseous precursor, based on the reactor volume, during phase (b2) may be at least 0.04 min^{-1} .

- 20 The gaseous precursor used in phase (b2) may be in admixture with an inert gas, for example, nitrogen or argon. Preferably, the admixture 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 gaseous precursor.

- 25 Operation at higher temperatures will increase the rate of the reaction and lead to faster deposition rate. The reactor temperature during phase (b2) is therefore preferably at least 320°C , or at least 340°C , or at least 35°C , or at least 360°C , or at least 365°C , or at least 370°C . However, excessive temperatures may reduce the control of the deposition resulting in the formation of undesirable coarse electroactive material domains and insufficient infiltration of the gaseous precursor into the pore structure of the porous particles. Accordingly, the reactor temperature during phase (b2) is preferably no more than no more than 500°C , more preferably no more than 450°C , more preferably no more than 420°C , more preferably no more than 395°C , more preferably no more than 390°C .

For example, the temperature during phase (b2) may be in the range from 320 to 500 °C, or from 320 to 450°C, or from 340 to 450°C, or from 350 to 420 °C, or from 360 to 400 °C, or from 365 to 395 °C, or from 370 to 390 °C, or from 380 to 390 °C.

5 The process of the invention is preferably operated under a regime where the gaseous precursor is supplied to the reactor at high concentration, or even in neat form. In order to control the rate of reaction and to achieve controlled infiltration of the gaseous precursor into the pore network of the porous particles, the reaction temperature in the phase (b2) is most preferably no more than 420 °C, or no more than 410 °C, or no more than 400 °C, or no more than 395 °C.

10 The pressure during phase (b2) is preferably in the range from 50 to 15000 kPa, or from 50 to 10000 kPa, or from 120 to 5000 kPa, or from 150 to 2000 kPa, or from 200 to 1600 kPa, or from 250 to 1500 kPa, or from 300 to 1200 kPa, or from 400 to 1000 kPa, or from 500 to 900 kPa, or from 600 to 800 kPa.

15 Where the pressure during phase (b2) is in the range from 1,500 kPa to 5,000 kPa (or 15,000 kPa), a preferred temperature range is from 360 °C to 400 °C, preferably 360 °C to 390 °C.

Where the pressure during phase (b2) is in the range from 700 kPa to less than 1,500 kPa (or 15,000 kPa), a preferred temperature range is from 370 °C to 410 °C, preferably 370 °C to 400 °C.

20 Where the pressure during phase (b2) is in the range from 200 kPa to less than 700 kPa (or 15,000 kPa), a preferred temperature range is from 380 °C to 450 °C, preferably 380 °C to 420 °C.

25 Where the pressure during phase (b2) is in the range from 50 kPa to less than 200 kPa (or 15,000 kPa), a preferred temperature range is from 400 °C to 550 °C, preferably 400 °C to 500 °C.

Operation at elevated pressure has the advantage of increasing the residence time of the gaseous precursor, thus increasing conversion even at lower temperatures.

Operation at low pressure has the advantage of providing very uniform deposition. However, the residence time of the precursor gas is reduced and therefore it is most

advantageous to use higher temperatures to ensure high consumption of the precursor gas (see above).

Operation at or near atmospheric pressure has the advantage of avoiding very high capital equipment investment on high pressure rated equipment.

- 5 The reactor preferably contains essentially no oxygen (or oxidizing gases) during phase (b2).

Step (b) preferably comprises agitating the porous particles during phase (b1) and/or during phase (b2). Preferably, the porous particles are agitated during both phase (b1) and phase (b2). Any suitable agitator may be used, such as a turbine agitator, a paddle agitator, an

- 10 anchor agitator, a propeller agitator, or a helical agitator.

- To maintain good control of the CVI process, an inverse relationship is preferably maintained between the temperature and pressure in phase (b2). In particular, where the pressure in the reactor is above 100 kPa, the reaction temperature in the reactor is preferably no more than 450 °C, more preferably no more than 430 °C, more 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.

Preferably, the temperature in the reactor during phase (b2) is in the range from 340 to 500 °C and the pressure in the reactor during phase (b2) is in the range from 600 to 5000 kPa.

- 20 Preferably, the temperature in the reactor during phase (b2) is in the range from 360 to 420 °C and the pressure in the reactor during phase (b2) is in the range from 600 to 2000 kPa.

Preferably, the temperature in the reactor during phase (b2) is in the range from 360 to 400 °C and the pressure in the reactor during phase (b2) is in the range from 700 to 2000 kPa.

Preferably, the temperature in the reactor during phase (b2) is in the range from 360 to 390 °C and the pressure in the reactor during phase (b2) is in the range from 1000 to 2000 kPa.

- 25 During phase (b2), the mole fraction of gaseous precursor in the reactor may be in the range from 0.2 to 0.8 by total moles of gaseous compounds in the reactor, or from 0.3 to 0.7, or from 0.4 to 0.6 by total moles of gaseous compounds in the reactor.

The total amount of electroactive material deposited in step (b) is preferably at least 26 wt%, or at least 28 wt%, or at least 30 wt%, or at least 32 wt%, or at least 34 wt%, or at least 36

wt%, or at least 38 wt%, or at least 40 wt%, or at least 42 wt%, or at least 44 wt%, based on the final weight of the composite particles obtained in step (b).

The total amount of electroactive material deposited in step (b) is preferably no more than 70 wt%, or no more than 68 wt%, or no more than 65 wt%, no more than 62 wt%, or no
5 more than 60 wt%, or no more than 58 wt%, or no more than 56 wt%, or no more than 54 wt%, based on the final weight of the composite particles obtained in step (b).

More preferably, the electroactive material is silicon and the composite particles obtained 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
10 least 38 wt% silicon, or at least 40 wt% silicon, or at least 42 wt% silicon, or at least 44 wt% silicon.

More preferably, the electroactive material is silicon and the composite particles obtained in step (b) comprise no more than 70 wt% silicon, or no more than 68 wt% silicon, or no more than 65 wt% silicon, no more than 62 wt% silicon, or no more than 60 wt% silicon, or
15 no more than 58 wt% silicon, or no more than 56 wt% silicon, or no more than 54 wt% silicon.

The amount of electroactive material deposited in step (b) is preferably selected such that at least 20% and up to 90% of the internal pore volume of the porous particles is occupied by the electroactive material following step (b). For example, the electroactive material may
20 occupy from 20% to 80%, or from 25% to 75%, or from 30% to 70%, or from 35 to 65%, or from 40 to 60%, or from 45% to 55% of the internal pore volume of the porous particles. Within these preferred ranges, the remaining pore volume of the porous particles is effective to accommodate expansion of the electroactive material during charging and discharging, without a large excess pore volume which does not contribute to the volumetric capacity of
25 the particulate particles. However, the amount of electroactive material is also not so high as to impede effective lithiation due to inadequate metal-ion diffusion rates or due to inadequate expansion volume resulting in mechanical resistance to lithiation.

In the case that the electroactive material is silicon, the amount of silicon deposited in step (b) can be related to the available pore volume in the porous particles by the optional
30 requirement that the weight ratio of deposited silicon to the porous particles in the range from $[0.5 \times P^1 \text{ to } 1.9 \times P^1]$: 1, wherein P^1 is a dimensionless quantity having the magnitude of the total pore volume of micropores and mesopores in the porous particles, as expressed

in cm^3/g (e.g. if the porous particles have a total volume of micropores and mesopores of $1.2 \text{ cm}^3/\text{g}$, then $P^1 = 1.2$). This relationship takes into account the density of silicon and the pore volume of the porous particles to define a weight ratio of silicon at which the pore volume is around 20% to 82% occupied. Preferably, the weight ratio of silicon deposited in step (b) to the porous particles is in the range from $[0.6 \times P^1 \text{ to } 1.8 \times P^1] : 1$ or from $[0.7 \times P^1 \text{ to } 1.7 \times P^1] : 1$, or from $[0.8 \times P^1 \text{ to } 1.6 \times P^1] : 1$.

The amount of silicon in the composite particles can be determined by elemental analysis. Preferably, elemental analysis is used to determine the elemental composition of the porous particles alone and the composition of the composite particles.

10 Silicon content is preferably determined by ICP-OES (Inductively coupled plasma-optical emission spectrometry). A number of ICP-OES instruments are commercially available, such as the iCAP® 7000 series of ICP-OES analysers available from ThermoFisher Scientific. The carbon content of the composite particles and of the porous carbon particles alone (as well as the hydrogen, nitrogen and oxygen content if required) are preferably
15 determined by IR absorption. A suitable instrument for determining carbon, hydrogen, nitrogen and oxygen content is the TruSpec® Micro elemental analyser available from Leco Corporation.

Preferably at least 90 wt%, more preferably at least 95 wt%, even more preferably at least 98 wt% of the electroactive material in the composite particles is located within the internal
20 pore volume of the porous particles such that there is no or very little electroactive material located on the external surfaces of the composite particles. As discussed above, deposition of electroactive material in a CVI process occurs at the surfaces of the porous particles. In view of the very high internal surface area of the porous particles, the reaction kinetics of the CVI process ensure that deposition of the electroactive material occurs almost entirely
25 within the pores of the porous particles.

The composite particles obtained 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 $30 \text{ m}^2/\text{g}$, or no more than $25 \text{ m}^2/\text{g}$, or no more than $20 \text{ m}^2/\text{g}$, or no more than $15 \text{ m}^2/\text{g}$, or no more than $10 \text{ m}^2/\text{g}$. In general, a low BET surface area is preferred in
30 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 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 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.

10 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 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:

$$20 \quad Y = 1.875 \times [(M_{\max} - M_{\min}) / M_f] \times 100\%$$

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 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.

The composite particles obtained 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.

- 5 The composite particles obtained 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:

10
$$Z = 1.875 \times [(M_f - M_{800}) / M_f] \times 100\%$$

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 .

- 15 Typically, the TGA analysis is carried out using a sample size of 10 mg $\pm$ 2 mg.

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.

- 20 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.
- 25 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.

- The process of the reaction may be carried out using any reactor that is capable of
- 30 operating in batch and continuous modes and at the specified reaction pressures and temperatures. Optionally, phases (b1) and (b2) may be carried out in different reactors,

with the particles being transferred between the reactors under a non-reactive atmosphere (e.g. an inert gas, or the by-product gases formed during the deposition process). If the process comprises phases (b1) both before and after phase (b2) then different reactors may optionally be used for the phase(s) (b1) before phase (b2) and
5 the phase(s) (b1) after phase (b2).

The reactor preferably induces the movement or mixing of the porous particles in the reaction zone that provides the conditions of temperature and pressure effective to cause deposition of the electroactive material into the pores of the porous particles.

The reactor is preferably a moving reactor, a moving bed, a reactor with moving stirring
10 elements, or a gas-traversed reactor, a fluidised bed reactor or a combination thereof.

The reactor may be a pressure reactor, generally, a reactor which can be operated in a manner such that the pressure inside the reactor is greater than the surrounding pressure of the reactor. The reactor may be a reactor operated under vacuum conditions below atmospheric pressure or at around atmospheric pressure. The reactor
15 may be a pressure reactor that may be operated at near atmospheric or vacuum conditions. The reactor can be operated horizontally, or vertically, or at an angle, or at a movable angle.

The reactor is preferably a type of reactor selected from the group comprising tubular reactors, fluidized bed reactors, pusher type furnace reactors, stirred tank reactors.
20 Particularly preferred are fluidized bed reactors and stirred tank reactors such as autoclave type reactors.

The reactor consisting on a moving reactor or a reactor with moving stirring elements may comprise a rotational movement. The one or more stirring elements may be selected from the group comprising helical stirrers, spiral stirrers, screw stirrers, anchor
25 stirrers, paddle stirrers and blade stirrers. The vertically operated reactor may comprise rotating elements from the group comprising helical stirrers, spiral stirrers, screw stirrers, anchor stirrers, blade stirrers and paddle stirrers. The horizontally operated reactor may comprise rotating elements from the group comprising ploughshare, paddle stirrers, blade stirrers, helical stirrers and spiral stirrers. Other ways of maintaining of

moving bed of particles during the CVI reaction include vibration, sonication and fluidisation techniques.

The reactor may have any desired geometry. Preferred forms of reactor construction are cylindrical, conical, frustoconical, spherical, drum reactors or tubular reactors, 5 double-cone, reactors with offset cones, V-shaped reactors, double-V-shaped reactors and polyhedral forms or combinations thereof. In the case of symmetrical forms of construction, the axis of rotation lies preferably in the axis of symmetry of the reactor. In the case of nonsymmetric forms of construction, the axis of rotation passes preferably through the center of gravity of the reactor. In another preferred embodiment, the axis 10 of rotation is selected such that a tumbling movement is developed. The mixing events within the moving bed reactor are preferably boosted by internals. Typical internals are guide plates, blades, vanes, and ploughshares.

The reactor may be a pressure reactor such an autoclave reactor comprising an internal stirrer. The internal stirrer may be a close-clearance stirrer. The close-clearance stirrer 15 may be a stirrer selected from the group of paddle stirrer, blade stirrer, helical stirrer, spiral stirrer, screw stirrer, anchor stirrer, ploughshare or combinations thereof. The close-clearance stirrer may be a helical close-clearance stirrer. Preferred stirring elements are elements which convey the bed material axially, tangentially or radially, or preferably combinations thereof.

20 The process of the invention optionally further comprises the step of:
(c) contacting the surface of the particles from step (b) with a passivating agent.

As defined herein, a passivating agent is a compound or mixture of compounds which is able to react with the surface of the electroactive material deposited in step (b) to 25 form a modified surface. In particular, a passivating agent as defined herein is a material which is able to react with the surfaces of the electroactive material to further reduce the surface energy thereof.

One type of passivation layer is a native oxide layer. A native oxide layer may be formed, for example, by exposing the electroactive material surface to a passivating 30 agent selected from air or another oxygen containing gas. The passivation layer may

comprise an oxide of the formula MO_x , wherein $0 < x \leq 2$. The oxide is preferably amorphous. The formation of a native oxide layer is exothermic and therefore requires careful process control to prevent overheating or even combustion of the particulate material. In the case that the passivating agent is an oxygen-containing gas, step (c) 5 may comprise cooling the material formed in step (b) to a temperature below 400 °C, preferably below 300 °C, optionally below 200 °C, optionally below 100 °C, prior to contacting the electroactive material surfaces with the oxygen containing gas.

Another type of passivation layer is a nitride layer that is formed, for example, by exposing the electroactive material surfaces to a passivating agent selected from ammonia or another nitrogen containing molecule. The passivation layer may comprise 10 a nitride of the formula MN_x , wherein $0 < x \leq 4/3$. The nitride is preferably amorphous. A nitride layer may be formed by contacting the electroactive material surfaces with ammonia at a temperature in the range from 200-700 °C, preferably from 400-700 °C, more preferably from 400-600 °C. The temperature may then be increased if necessary 15 into the range of 500 to 1,000 °C to form a nitride surface. Nitride passivation may be preferred to oxide passivation. As sub-stoichiometric nitrides (such as SiN_x , wherein $0 < x \leq 4/3$) are conductive, nitride passivation layers may function as a conductive network that allows for faster charging and discharging of the electroactive material. Phosphine may also be used as a passivating agent, as a phosphorus analog of ammonia. 20

Another type of passivation layer is an oxynitride layer that is formed, for example, by exposing the electroactive material surfaces to a passivating agent comprising ammonia (or another nitrogen containing molecule) and oxygen gas. The passivation layer may comprise an electroactive material oxynitride of the formula MO_xN_y , wherein 25 $0 < x < 2$, $0 < y < 4/3$, and $0 < (2x+3y) \leq 4$. The oxynitride is preferably amorphous.

Another type of passivation layer is a carbide layer. The passivation layer may comprise a carbide of the formula MC_x , wherein $0 < x \leq 1$. The carbide is preferably amorphous. A carbide layer may be formed by contacting the electroactive material surfaces with a passivating agent selected from carbon containing precursors, e.g. methane or ethylene 30 at elevated temperatures, e.g. in the range from 250 to 700 °C. At lower temperatures, covalent bonds are formed between the electroactive material surfaces and the carbon-containing precursors, which are then converted to a monolayer of crystalline carbide as

the temperature is increased. The carbide may comprise a silicon carbide of the formula SiC_x , wherein $0 < x \leq 1$.

Other suitable passivating agents include compounds comprising an alkene, alkyne or carbonyl functional group, more preferably a terminal alkene, terminal alkyne, aldehyde
5 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) $\text{O=CR}^1\text{R}^1$;

10 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.

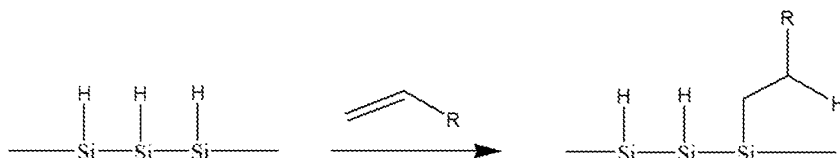
Particularly preferred passivating agents include one or more compounds of the
15 formulae:

- (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,
20 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 (e.g. Si-H groups) at the electroactive
25 material surface to form a covalently passivated surface which is resistant to oxidation by air. For example, the passivation reaction between a silicon surface and the passivating agent may therefore 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

5 hydride groups at the electroactive material surfaces is understood to result in elimination of H₂ and the formation of a direct bond between X and the electroactive material surfaces.

Suitable passivating agents in this category include compounds of the formula

- (iv) HX-R², and
- 10 (v) HX-C(O)-R¹,

wherein X represents O, S, NR¹ or PR¹; each R¹ is independently as defined above; and R² represents an unsubstituted or substituted aliphatic or aromatic hydrocarbyl group having from 1 to 20 carbon atoms, or R¹ and R² together form an unsubstituted or substituted ring structure comprising from 3 to 8 carbon atoms in the ring. Preferably

15 X represents O or NH.

Preferably R² 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.

20 Contacting of the electroactive material with the passivating agent in step (c) may be carried out at a temperature in the range of 25 to 500 °C, preferably at a temperature in the range of from 50 to 450 °C, more preferably from 100 to 400 °C.

Step (c) is carried out following step (b). However, it is not excluded that corresponding passivation steps may be carried out between phases (b1) and (b2) of step (b).

25 The process of the invention optionally further comprises the step of:

(d) subjecting the particles from step (b) or step (c) to heat treatment at a temperature of at least 400 °C and in the presence of an inert gas.

This heat treatment is thought to promote the elimination of hydrogen and the solid-state rearrangement of the electroactive material (e.g. silicon) atoms, thereby reducing the density of unstable and reactive Si-H bonds and promoting the formation of more thermodynamically stable Si-Si bonds. This is believed to contribute to improved stability of the electroactive material during charging and discharging and therefore to an improvement in the cycle life of metal-ion batteries comprising the composite particles.

The temperature during step (d) is generally greater than the maximum temperature in step (b). Preferably, the temperature during step (d) is at least 20 °C, or at least 40 °C, or at least 60 °C, or at least 80 °C, or at least 100 °C, or at least 120 °C, or at least 140 °C, or at least 150 °C greater than the temperature in step (b).

Step (d) is carried out in the presence of an inert gas. An inert gas refers herein to any gas that does not undergo reaction under the prevailing reaction conditions. Preferably, the inert gas is selected from nitrogen and the noble gases, in particular argon. Optionally, the inert gas may comprise hydrogen. The inert gas may be selected from the group consisting of nitrogen, argon, helium and combinations thereof.

Step (d) is optionally carried out before step (c). One effect of step (d) is to reopen pore spaces that were previously obstructed or capped by electroactive material nanostructures, such that the pore spaces are accessible to passivating gases, thus allowing for a more extensive passivation of the electroactive material surfaces and the reduction or elimination of hydrogen-terminated electroactive material surfaces.

The process of the invention optionally further comprises the step of:

(e) contacting the composite particles from step (b) or step (c) or step (d) 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.

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.

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.

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.

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;
- (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.

- 5 In a second aspect, the invention provides composite particles that are obtainable by the process of the first aspect.

In a third aspect, the invention provides a process for preparing an electrode, the process comprising the steps of:

- (a) combining the composite particles of the second aspect with an aqueous liquid and
10 at least one binder;
(b) casting the slurry onto a current collector;
(c) drying the cast slurry to form a coating layer on the current collector.

As used herein, the term current collector refers to any conductive substrate that is capable of carrying a current to and from the electroactive particles in the composition. Examples
15 of materials that can be used as the current collector include copper, aluminium, stainless steel, nickel, titanium and sintered carbon. Copper is a preferred material. The current collector is typically in the form of a foil or mesh having a thickness of between 3 to 500 μm . The particulate materials of the invention may be applied to one or both surfaces of the current collector to a thickness which is preferably in the range from 10 μm to 1 mm, for
20 example from 20 to 500 μm , or from 50 to 200 μm .

The electrode is fabricated by combining the composite particles an aqueous liquid, at least one binder and optionally one or more viscosity modifying additives to form a slurry. The slurry is then cast onto the surface of a current collector and the solvent is removed, thereby forming an electrode layer on the surface of the current collector. Further steps, such as
25 heat treatment to cure any binders and/or calendering of the electrode layer may be carried out as appropriate. The electrode layer suitably has a thickness in the range from 20 μm to 2 mm, preferably 20 μm to 1 mm, preferably 20 μm to 500 μm , preferably 20 μm to 200 μm , preferably 20 μm to 100 μm , preferably 20 μm to 50 μm .

In an alternative process, the slurry formed in step (a) may be formed into a freestanding
30 film or mat comprising the particulate material of the invention, for instance by casting the slurry onto a suitable casting template, removing the solvent and then removing the casting

template. The resulting film or mat is in the form of a cohesive, freestanding mass that may then be bonded to a current collector by known methods.

Examples

5 Table 1 presents experimental examples of the process of the invention using an initiation step (b1), a continuous deposition step (b2) and an optional termination step (b1). The porous particles had:

- (i) a D_{50} particle diameter of 7.4 μm ;
- (ii) a total pore volume of micropores and mesopores as measured by gas
10 adsorption of 0.72 cm^3/g , of which the micropore volume is 0.50 cm^3/g ;
- (iii) a PD_{50} pore diameter of 1 nm;
- (iv) a BET surface area of 1667 m^2/g .

A stirred autoclave reactor was filled with the specified quantity of porous carbon particles. The reactor was sealed and slowly placed under vacuum (10 mbar) to remove the air and
15 then filled with dry nitrogen or argon that was free of oxygen. The process was repeated three times to expel all of the air from the porous carbon particles.

Initiation phase (b1)

The reactor was evacuated again, and then filled with the specified amount of silane. The reactor was then stirred at 60 rpm, heated to the specified temperature at a ramp rate of
20 10°C /min and held at that temperature for one hour. The pressure was monitored such that it did not exceed 50MPa. After one hour, the reactor was slowly depressurised to the pressure in the continuous phase (b2).

Continuous phase (b2)

The reactor temperature and pressure were adjusted as set out in Table 1. A continuous
25 flow of silane-containing gas was then supplied to the reactor at the specified flow rate (diluted with nitrogen where indicated) while stirring at 60 rpm. Effluent gases from the reactor were throttled as necessary to maintain the specified pressure. Once the required amount of silicon deposition was obtained, the gas flow was switched to nitrogen and the reactor was cooled below 300°C

Termination phase (b1) – if used

The reactor was evacuated again, and then filled with the specified amount of silane. The reactor was then stirred at 60 rpm, heated to the specified temperature at a ramp rate of 10°C /min and held at that temperature for one hour. The pressure was monitored such
5 that it did not exceed 50MPa. After one hour, stirring was stopped and the reactor was slowly depressurised.

Following the continuous phase (b2) or the termination phase (b1) (if used), the reactor was depressurised and filled with nitrogen then cooled to below 30 °C. The composite particle product was then passivated with air by using a mixture of 10% air in nitrogen by
10 evacuating the reactor and filling it with the gas to a pressure of 0.1 MPa and allowing it to stand for 15 minutes. This process was repeated 3 times using the mixture of 10% air in nitrogen, 3 times using 25% air in nitrogen, once with 50% air in nitrogen, once with 75% air in nitrogen, and finally with 100% air. The composite particles were then removed from the reactor.

TABLE1

Example No.	1	2	3	4	5	6	7	8	9	10
Porous particle charge (g _{PP} /L _{RV}) ^a	150	200	200	200	50	300	100	270	270	150
Initiation phase (b1)										
Silane charge (g _S /L _{RV}) ^b	11.7	17.5	11.7	0.58	0.58	4.1	4.7	4.6	4.6	11.7
Silane charge (g _S /Kg _{PP}) ^c	78	88	58.3	2.9	12	14	47	17	17	78
Silicon precursor gas concentration (mol%)	100	100	100	100	100	100	100	100	100	100
Reactor temperature (°C)	360	360	360	440	450	390	390	390	390	360
Si wt% of total composite	7	8	5.4	0.3	1	1	4	2	2	7
Continuous phase (b2)										
Silane flow rate (g _S /min/Kg _{PP})	2.0	7.0	2.0	2.0	28	4.7	10	1.5	1.5	6.7
Space time (min) ^d	5.6	4.6	0.67	0.67	0.57	2.95	4.6	11.6	11.6	4.4
Space velocity (min ⁻¹) ^e	0.18	0.22	1.49	1.48	1.4	0.27	0.22	0.09	0.09	0.23
Reactor Temperature (°C)	420	390	450	440	450	390	390	390	390	420
Reactor Pressure (KPa)	300	1100	50	50	150	710	800	800	800	800
Silicon precursor gas concentration (mol%)	100	100	100	100	80	80	100	100	100	100

^a Porous particle charge to the reactor in grams of porous particles (g_{PP}) per litre of reactor volume (L_{RV})

^b Silane (silicon precursor gas) charge to the reactor in phase (b1) in grams of silicon (g_S) per litre of reactor volume (L_{RV})

^c Silane (silicon precursor gas) charge to the reactor in phase (b1) in grams of silicon (g_S) per Kg of porous particles (Kg_{PP})

^d reactor vol (L) divided by the flow rate of gas (gaseous precursor and any diluent gases) in L/min

^e flow rate of gaseous precursor (excluding any diluent gases) in L/min divided by reactor vol (L)

TABLE 1 (Continued)

Example No.	1	2	3	4	5	6	7	8	9	10
Termination phase (b1)										
Silicon precursor gas charge (g _{Si} /L _{RV})	-	-	-	-	-	-	-	-	4.6	7.6
Silicon precursor gas charge (g _{Si} /Kg _{pp})	-	-	-	-	-	-	-	-	17	50.6
Silicon precursor gas concentration (mol%)	-	-	-	-	-	-	-	-	100	100
Reactor Temperature (°C)	-	-	-	-	-	-	-	-	390	395
Si wt% of total composite	-	-	-	-	-	-	-	-	1.6	4.7
Final product										
Silicon in final product (wt%)	44	54	35	65	30	40	50	60	55	45
g _{Si} /Kg _{pp} in final product	0.79	1.17	0.54	1.86	0.43	0.67	1.00	1.50	1.22	0.82

CLAIMS

1. A process for preparing composite particles, the process comprising the steps of:
 - (a) providing a charge of porous particles in a reactor;
 - (b) contacting the porous particles with a gaseous precursor of an electroactive material
- 5 in a reactor under conditions of temperature and pressure effective to cause deposition of the electroactive material into the pores of the porous particles to form the composite particles;
wherein step (b) comprises:
 - (b1) at least one discontinuous deposition phase during which the charge of
 - 10 porous particles is contacted with a charge of the gaseous precursor and the reactor is then sealed during deposition of the electroactive material; and
 - (b2) a continuous deposition phase during which the porous particles are contacted with the gaseous precursor in a reactor, wherein the gaseous precursor is supplied to the reactor continuously during deposition of the electroactive
 - 15 material.
2. A process according to claim 1, wherein the first phase of step (b) is a discontinuous phase (b1).
3. A process according to claim 2, wherein up to 10wt% of the total electroactive material deposited in step (b) is deposited in said first phase.
- 20 4. A process according to any preceding claim, wherein the last phase of step (b) is a discontinuous phase (b1).
5. A process according to claim 4, wherein up to 10wt% of the total electroactive material deposited in step (b) is deposited in said last phase.
6. A process according to claim 4 or claim 5, wherein step (b) comprises three phases
- 25 in which the first phase is a discontinuous phase (b1), the second phase is a continuous phase (b2) and the third phase is a discontinuous phase (b1).
7. A process according to any preceding claim, wherein the charge of the porous particles in step (a) has a mass of at least 20 g per litre of reactor volume (g/L_{RV}), or at least 50 g/L_{RV}, or at least 80 g/L_{RV}, or at least 100 g/L_{RV}, or at least 150 g/L_{RV}, or at least 200
- 30 g/L_{RV}, or at least 250 g/L_{RV}.

8. A process according to any preceding claim, wherein the electroactive material is silicon and the gaseous precursor is a silicon precursor gas.
9. A process according to claim 8, wherein the charge of silicon precursor gas used in phase (b1) comprises at least 0.5 g/L_{RV} of silicon, at least 1 g/L_{RV} silicon, at least 2 g/L_{RV} silicon, at least 3 g/L_{RV} silicon, at least 4 g/L_{RV} silicon, at least 5 g/L_{RV} of silicon, or at least 10 g/L_{RV} of silicon, or at least 20 g/L_{RV} of silicon, or at least 40 g/L_{RV} of silicon, or at least 60 g/L_{RV} of silicon, or at least 80 g/L_{RV} of silicon, or at least 100 g/L_{RV} of silicon.
10. A process according to claim 8 or claim 9, wherein the charge of silicon precursor gas in phase (b1) comprises at least 2 g silicon per kg of the porous particles, or at least 3 g silicon per kg of the porous particles, or at least 5 g silicon per kg of the porous particles, or at least 10 g silicon per kg of the porous particles, or at least 20 g silicon per kg of the porous particles, or at least 30 g silicon per kg of the porous particles, or at least 40 g silicon per kg of the porous particles, or at least 50 g silicon per kg of the porous particles.
11. A process according to any preceding claim, wherein the charge of the gaseous precursor in phase (b1) is in admixture with an inert gas, preferably wherein the admixture 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 gaseous precursor.
12. A process according to any preceding claim, wherein the temperature in phase (b1) is in the range from 320 to 500 °C, or from 340 to 450 °C, or from 350 to 420 °C, or from 360 to 340 °C, or from 365 to 395 °C, or from 370 to 390 °C.
13. A process according to any preceding claim, wherein the pressure in phase (b1) is at least 100 kPa, or at least 110 kPa, or at least 120 kPa, or at least 150 kPa, or at least 200 kPa, or at least 300 kPa, or at least 500 kPa, or at least 600 kPa, or at least 700 kPa, or at least 800 kPa, or at least 900 kPa, or at least 1,000 kPa.
14. A process according to any preceding claim, wherein the gaseous precursor is a silicon precursor gas and the flow rate of the silicon precursor gas into the reactor in phase (b2) in grams of silicon per minute per kg of the porous particles ($\text{g}_{\text{Si}} \cdot \text{min}^{-1} \cdot \text{kg}_{\text{PP}}^{-1}$) is from 0.2 to 25 $\text{g}_{\text{Si}} \cdot \text{min}^{-1} \cdot \text{kg}_{\text{PP}}^{-1}$, or from 0.5 to 20 $\text{g}_{\text{Si}} \cdot \text{min}^{-1} \cdot \text{kg}_{\text{PP}}^{-1}$, or from 1 to 15 $\text{g}_{\text{Si}} \cdot \text{min}^{-1} \cdot \text{kg}_{\text{PP}}^{-1}$,

or from 1 to 14 $\text{g}_{\text{Si}} \cdot \text{min}^{-1} \cdot \text{kg}_{\text{PP}}^{-1}$, or from 1 to 13 $\text{g}_{\text{Si}} \cdot \text{min}^{-1} \cdot \text{kg}_{\text{PP}}^{-1}$, or from 1 to 12 $\text{g}_{\text{Si}} \cdot \text{min}^{-1} \cdot \text{kg}_{\text{PP}}^{-1}$, or from 2 to 12 $\text{g}_{\text{Si}} \cdot \text{min}^{-1} \cdot \text{kg}_{\text{PP}}^{-1}$.

15. A process according to any preceding claim, wherein the space time of the gaseous precursor in contact with the porous particles in phase (b2) is maintained in the range from 0.2 to 60 min, or from 0.5 to 60 min, or from 1 to 60 min, or from 2 to 45 min, or from 3 to 30 min, or from 4 to 25 min, or from 5 to 20 min.

16. A process according to any preceding claim, wherein the space velocity of the gaseous precursor, based on the reactor volume, during phase (b2) is at least 0.02 min^{-1} , or at least 0.025 min^{-1} , or at least 0.03 min^{-1} , or at least 0.035 min^{-1} , or at least 0.04 min^{-1} , or at least 0.045 min^{-1} , or at least 0.05 min^{-1} , or at least 0.06 min^{-1} , or at least 0.07 min^{-1} , or at least 0.08 min^{-1} , or at least 0.09 min^{-1} , or at least 0.1 min^{-1} , or at least 0.15 min^{-1} , or at least 0.2 min^{-1} , or at least 0.25 min^{-1} , or at least 0.3 min^{-1} , or at least 0.35 min^{-1} , or at least 0.4 min^{-1} , or at least 0.5 min^{-1} , or at least 0.7 min^{-1} , or at least 1 min^{-1} , or at least 1.5 min^{-1} .

17. A process according to any preceding claim, wherein the space velocity of the gaseous precursor, based on the reactor volume, during phase (b2) is no more than 3 min^{-1} , or no more than 2 min^{-1} , or no more than 1.5 min^{-1} , or no more than 1 min^{-1} , or no more than 0.8 min^{-1} , or no more than 0.75 min^{-1} , or no more than 0.7 min^{-1} , or no more than 0.65 min^{-1} , or no more than 0.6 min^{-1} , or no more than 0.55 min^{-1} , or no more than 0.5 min^{-1} .

18. A process according to any preceding claim, wherein the concentration of the gaseous precursor in the gas supplied to the reactor in phase (b2) 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%.

19. A process according to any preceding claim, wherein the temperature in phase (b2) is in the range from 320 to 500 °C, or from 340 to 450 °C, or from 350 to 420 °C, or from 360 to 400 °C, or from 365 to 395 °C, or from 370 to 390 °C.

20. A process according to any preceding claim, wherein the pressure in phase (b2) is in the range from 50 to 15000 kPa, or from 50 to 10000 kPa, or from 120 to 5000 kPa, or from 150 to 2000 kPa, or from 200 to 1600 kPa, or from 250 to 1500 kPa, or from 300 to 1200 kPa, or from 400 to 1000 kPa, or from 500 to 900 kPa, or from 600 to 800 kPa.

21. A process according to any preceding claim, wherein the reactor contains essentially no oxidizing gas during step (b).
22. A process according to any preceding claim, wherein the porous particles comprise micropores and/or mesopores.
- 5 23. A process according to any preceding claim, 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.
- 10 24. A process according to any preceding claim, wherein the precursor gas in phase (b1) and/or phase (b2) is selected from silane (SiH_4), disilane (Si_2H_6), trisilane (Si_3H_8), and tetrasilane (Si_4H_{10}), preferably wherein the same silicon precursor gas is used in phase (b1) and phase (b2), preferably where the silicon precursor gas used in phase (b1) and phase (b2) is silane.
- 15 25. A process according to any preceding claim, wherein phase (b1) and/or phase (b2) comprises agitating the porous particles, preferably mechanically agitating the porous particles, preferably continuously mechanically agitating the porous particles.
26. A process according to any preceding claim, wherein phase (b2) comprises:
- (i) continuously withdrawing the effluent gas from the pressure reactor; or
 - 20 (ii) semi-continuously withdrawing the effluent gas from the pressure reactor.
27. 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.
- 25 28. A process according to any preceding claim, wherein the composite particles formed in step (b) comprise no more than 70 wt% silicon, or no more than 68 wt% silicon, or no more than 65 wt% silicon, 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

29. A process according to any preceding claim, wherein the process further comprises the step of:

(c) contacting the composite particles with a passivating agent under conditions that are effective to passivate the composite particles from step (b).