

Process for the Preparation of Silicon-Containing Composite Particles

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

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

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

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

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

intercalation of lithium into bulk silicon results in expansion of the silicon material by up to 400% of its original volume which can lead to failure of the battery. Repeated charge-discharge cycles cause significant mechanical stress, resulting in fracturing and delamination of the silicon. The formation of a solid electrolyte interphase (SEI) layer on the silicon surface consumes the electrolyte and newly exposed silicon surfaces on fracture surfaces results in further electrolyte decomposition and increased thickness of the SEI layer and irreversible consumption of lithium. These failure mechanisms collectively result in an unacceptable loss of electrochemical capacity over successive charging and discharging cycles.

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

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

CVI processes can be operated in batch or continuous mode with respect to the silicon precursor.

- 5 In systems that are operated by batch dosing of silicon precursor, several cycles of CVI deposition are necessary to obtain composite particles with the required content of silicon. At the beginning of each cycle, a charge of silicon precursor is introduced into the reactor. The reactor temperature generally decreases as silicon precursor is added, necessitating heating of the reactor to return the feedstock to reaction temperature. Removal of by-product gases after each cycle is also required. Consequently, the overall manufacturing time of the composite particles is long and the throughput of such systems is poor. These systems are therefore ill-suited to scale-up and producing large quantities of material is difficult.

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

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

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

- In systems that are operated by continuous addition of silicon precursor, it has been found that the conversion of silicon precursor does not remain constant, but rather changes over the course of the CVI reaction, hence the conversion of silicon precursor becomes suboptimal, thus leading to process inefficiency.

Conversion of silicon precursor can be controlled by balancing mass transfer requirements of silicon precursor gas and porous particles with the reaction kinetics. One way of achieving this balance is to change the temperature of the CVI process over the course of the CVI reaction. However, it has been found that changing the temperature results in significantly increased process time due to the time needed to heat and cool reactors.

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

- 10 (a) providing a plurality of porous particles in a reactor;
 - (b) contacting the plurality of porous particles with a silicon precursor gas at conditions effective to cause deposition of silicon in the pores of the porous particles;
 - (c) measuring the composition of an effluent gas withdrawn from the reactor;
 - (d) detecting a change in the composition of the effluent gas;
 - 15 (e) adjusting at least one gas outlet of the reactor to adjust the flow rate of the effluent gas to increase the pressure in the reactor in response to the detected change in the composition of the effluent gas and continuing deposition of silicon in the pores of the porous particles at the adjusted pressure;
- to provide composite particles comprising a porous particle framework and silicon within the pores of the porous particle framework;
- 20 wherein the silicon precursor gas is introduced into the reactor continuously during steps (b) to (e).

The invention therefore relates in general terms to a process for preparing a composite particulate material in which silicon is deposited into the pore network of porous particles by a process of chemical vapour infiltration (CVI), i.e. via the thermal decomposition of a silicon-containing precursor compound. The composite particles therefore comprise a first component in the form of the porous particles, these forming a framework that supports a second component in the form of a plurality of silicon domains that are disposed within the pore structure of the porous particle framework. As used herein, the term "silicon domain" refers to a body of silicon having maximum dimensions that are determined by the location of the silicon within the pore structure of the porous particles.

Batch operation can take a relatively long time to complete infiltration of silicon into the porous particles. In batch operation the deposition reaction kinetics slow down as the reaction proceeds, for example due to the increased by-product gas concentration. A further factor that contributes to the long synthesis time in batch operation is that it can involve multiple cycles and inherently involves production downtime due to silicon precursor gas loading prior to reaction and the release of the product gases after reaction. The process according to the invention is believed to result in increased throughput by reducing production downtime associated with fluctuations in temperature that are inherent in systems that are operated by batch dosing of silicon precursor gas and in systems that intentionally vary temperature, whilst also enabling the processing of large batches of composite particles. The process according to the invention, even when supplying silicon precursor at low flow rates, does not suffer from slowing down of the reaction kinetics as a controlled concentration of the silicon precursor gas in the reactor can be sustained. Further, downtime outside of the reaction attributed to silicon precursor gas loading prior to reaction and the release of the product gases after reaction, necessary for batch operation, is eliminated. Overall, the process according to the invention can prepare similar silicon composite particles to a batch operation in a total time that is between a half to a tenth of the duration of the batch infiltration or even lower.

The process according to the invention involves adjusting at least one gas outlet of the reactor to adjust the flow rate of the effluent gas to increase the pressure in the reactor in response to detecting a change in the composition of an effluent gas withdrawn from the reactor. Deposition of silicon in the pores of the porous particles is continued at the adjusted pressure, meaning that deposition is not stopped between steps (b) and (e). Increasing the pressure in the reactor increases the residence time of the silicon precursor gas in the reactor. Increasing the residence time of the silicon precursor gas in the reactor optimises conversion of silicon precursor. The pressure in the reactor can be adjusted more quickly than the temperature of the reactor, thus adjusting the pressure in the reactor to optimise conversion of silicon precursor enables a more efficient process. Thus, the invention maintains high conversion of silicon precursor whilst significantly increasing throughput compared to batch operation.

Operating the reactor under these conditions means that the CVD deposition proceeds under conditions where fresh silicon precursor is added before by-products are removed fully from the system. Thus, as the silicon precursor gas is continuously added to the reactor it mixes with by-products. Compared to systems that are operated by batch dosing of silicon

precursor gas, the porous particles are contacted by a more consistent concentration of silicon precursor throughout the deposition.

The degree of control over the deposition reaction is enhanced as gradients of temperature and concentration of silicon precursor in the reactor can be reduced, such that the porous particles are exposed to more consistent conditions. Increased control of the reaction conditions could result in better control of important properties of the composite particles, including silicon content, surface area and amount of coarse silicon.

The process according to the present invention also achieves an optimal balance between conversion and utilisation of the silicon precursor. The present invention can avoid excess silicon precursor gas being introduced into the reactor whilst increasing pressure because the invention involves adjusting the flow rate of the effluent gas to increase the pressure in the reactor. Whilst it is possible to increase the pressure in the reactor by increasing the flow rate of the silicon precursor gas into the reactor, this change alone would result in excess silicon precursor gas being introduced into the reactor, leading to a decrease in utilisation of the silicon precursor. Moreover, safety concerns may arise as to the ability to control the pressure within the reactor through input of gas alone.

OPERATION

The process is operated as continuous with respect to the silicon precursor gas and batch with respect to the porous particles. Therefore the reactor operates as a semi-batch reactor.

The term continuous is used herein to distinguish from batch-type operation. In a batch operation, a batch of the starting material (porous particles) is added to the reactor in a first step, the reaction is allowed to progress for a specified period, and then a batch of product (composite particles) is withdrawn from the reactor. In a continuous operation, the introduction of the starting material (silicon precursor) into the reactor, and optionally the withdrawal of the product (effluent gas), occurs continuously with the reaction in progress.

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

The effluent gas withdrawn from the reactor comprises at least one by-product gas from the CVI reaction and optionally unreacted silicon precursor. For example, when the silicon precursor is silane, disilane or trisilane, the deposition reaction produces hydrogen (H₂) as a by-product. The effluent gas may comprise silicon precursor, at least one by-product gas and optionally other gases such as an inert gas (such as nitrogen or argon). In a particularly preferred embodiment, the silicon precursor is silane and the by-product gas is hydrogen.

Methods for measuring the composition of an effluent gas withdrawn from the reactor are known to the skilled person and include but are not limited to gas chromatography, mass spectrometry and infrared spectroscopy, such as Fourier-transform infrared spectroscopy (FT-IR).

As used herein, a "change in the composition of the effluent gas" means a deviation in the concentration of one or more components of the effluent gas. The deviation in concentration may be a percent deviation of at least 1 %, or at least 2 %, or at least 3 %, or at least 4 %, or at least 5 %. The deviation in concentration may be a percent deviation of no more than 10 %, or no more than 9 %, or no more than 8 %, or no more than 7 %, or no more than 6 %.

The pressure in the reactor may be increased in response to detecting an increase in the concentration of the silicon precursor in the effluent gas. The pressure in the reactor may be increased in response to detecting an increase of at least 1 % in the concentration of the silicon precursor in the effluent gas, or at least 2 %, or at least 3 %, or at least 4 %, or at least 5 %. The pressure in the reactor may be increased in response to detecting an increase of no more than 10 % in the concentration of the silicon precursor in the effluent gas, or no more than 9 %, or no more than 8 %, or no more than 7 %, or no more than 6 %.

The pressure in the reactor may be increased in response to detecting a decrease in the concentration of a by-product gas in the effluent gas. When the silicon precursor is silane, the by-product gas is hydrogen. The pressure in the reactor may be increased in response to detecting a decrease of at least 1 % in the concentration of the by-product gas in the effluent gas, or at least 2 %, or at least 3 %, or at least 4 %, or at least 5 %. The pressure in the reactor may be increased in response to detecting a decrease of no more than 10 % in the concentration of the by-product gas in the effluent gas, or no more than 9 %, or no more than 8 %, or no more than 7 %, or no more than 6 %.

Both the concentration of the silicon precursor and the concentration of the by-product gas in the effluent gas may be measured and the pressure in the reactor may be increased accordingly.

5 The skilled person will be aware of suitable gas outlets, which include but are not limited to flow control valves and back pressure valves.

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

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

15 The effluent gas may be withdrawn from the reactor continuously. In this embodiment, both the supply of the silicon precursor gas and the withdrawal of effluent gas from the reactor occur continuously and simultaneously with the reaction in progress.

Alternatively, the effluent gas may be withdrawn from the reactor semi-continuously. As used herein, semi-continuously means that the effluent gas is removed intermittently.

20 Semi-continuous withdrawal of the effluent gas from the reactor may be achieved by oscillating the at least one gas outlet of the reactor between an open state and a closed state.

The at least one gas outlet may comprise a membrane separator that preferentially allows the at least one by-product gas to exit the reactor and prevents the silicon precursor from
25 exiting the reactor.

A flow regulator device may be used to regulate the flow rate of silicon precursor gas introduced into the reactor. Suitable flow regulator devices include but are not limited to a reverse pressure controller, an orifice or other fast acting mechanism.

It will be appreciated by those skilled in the art that the units of measurement for the flow rate of the effluent gas are not particularly limited, provided that adjustment of the flow rate of the effluent gas is sufficient to increase the pressure in the reactor. The flow rate of the effluent gas may be a mass flow rate or a volumetric flow rate. For example, flow rate of the effluent gas may be defined herein in terms of: grams of silicon in the silicon precursor per minute per kilogram of porous particles ($\text{gmin}^{-1}\text{kg}^{-1}$) and/or grams of silicon in the silicon precursor per minute per litre of reactor volume ($\text{gmin}^{-1}/\text{L}_{\text{RV}}$).

Step (e) comprises continuing deposition of silicon in the pore of the porous particles at the adjusted pressure. Therefore, the conditions in the reactor in step (e) are effective to cause deposition of silicon in the pores of the porous particles. This continuation of deposition may be referred to as a dwell period. After the dwell period, a change in the composition of the effluent gas may be detected, so steps (c) to (e) may be repeated. The process may include more than one adjustment of the at least one gas outlet of the reactor to adjust the flow rate of the effluent gas to increase the pressure in the reactor in response to the detected change in the composition of the effluent gas. Therefore, the process may comprise repeating steps (c) to (e) one or more times.

In this way, the pressure in the reactor may be adjusted in response to detected changes in the composition of the effluent gas throughout the duration of the CVI reaction to ensure optimal conversion of silicon precursor.

As used herein, "conversion" as in "conversion of silicon precursor" generally refers to the instantaneous conversion. That is, the conversion at a given point in time during the synthesis of the composite particles, and the given point in time may be a time period, such as 5 seconds, or 10 seconds, or 30 seconds, or 60 seconds. As used herein, "utilization" as in "utilization of silicon precursor" generally refers to the overall conversion for the whole synthesis of the composite particles.

Step (d) may further comprise:

calculating the conversion of the silicon precursor;

comparing the calculated conversion of silicon precursor with a target conversion of silicon precursor; and

determining that the calculated conversion of silicon precursor is less than the target conversion of silicon precursor;

and step (e) further comprises increasing the pressure in the reactor such that the conversion of silicon precursor is increased to at least the target conversion of silicon precursor.

5 Methods for calculating the conversion of the silicon precursor will be known to the skilled person. For example, the conversion of the silicon precursor may be calculated based on the known amount of silicon precursor that is introduced into the reactor (SP_{in}) and the measured amount of silicon precursor that is withdrawn from the reactor (SP_{out}). That is, conversion may be calculated as $(SP_{in}-SP_{out})/SP_{in}$ expressed as a percentage. The known amount of silicon precursor that is introduced into the reactor (SP_{in}) and the measured amount of silicon precursor that is withdrawn from the reactor (SP_{out}) can be measured
10 substantially contemporaneously to calculate the conversion at a given time. The calculated conversion of the silicon precursor may be an arithmetic mean of conversions measured across a period of time, such as more than one second or up to a minute.

The amount of silicon precursor can be measured directly using known methods, such as
15 gas chromatography, mass spectrometry and infrared spectroscopy, such as Fourier-transform infrared spectroscopy (FT-IR). The amount of silicon precursor can also be measured indirectly by measuring the amount of a by-product of the silicon deposition reaction (such as hydrogen when the silicon precursor is silane) because the by-product evolution is directly linked to the silicon precursor gas reacted. For example, one silane
20 molecule reacts to form two molecules of hydrogen in a silicon deposition reaction. The amount of hydrogen can be measured using known methods, such as thermal conductivity and/or gas chromatography.

The target conversion of silicon precursor is a predetermined aim for the conversion of silicon precursor, i.e. the instantaneous conversion. The target conversion of silicon precursor may be varied during the synthesis of the composite particles. Alternatively, the
25 target conversion of silicon precursor may be the same throughout the whole synthesis of the composite particles. The target conversion of silicon precursor may be at least 60 %, or at least 70 %, or at least 80 %, or at least 90 %, or at least 95 %, or at least 97 %, or at least 99 %, or 100 %.

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

The pressure in the reactor may be increased by at least $[50 \text{ kPa} \times \Delta X]$, wherein ΔX represents the difference between the calculated conversion of silicon precursor in % and

the target conversion of silicon precursor in %. The pressure in the reactor may be increased by at least $[60 \text{ kPa} \times \Delta X]$, or at least $[70 \text{ kPa} \times \Delta X]$, or at least $[80 \text{ kPa} \times \Delta X]$, or at least $[90 \text{ kPa} \times \Delta X]$, or at least $[100 \text{ kPa} \times \Delta X]$.

- The pressure in the reactor may be increased by no more than $[3000 \text{ kPa} \times \Delta X]$, or no more than $[2000 \text{ kPa} \times \Delta X]$, or no more than $[1000 \text{ kPa} \times \Delta X]$, or no more than $[500 \text{ kPa} \times \Delta X]$, or no more than $[400 \text{ kPa} \times \Delta X]$, or no more than $[300 \text{ kPa} \times \Delta X]$, or no more than $[200 \text{ kPa} \times \Delta X]$.

Step (d) may further comprise:

calculating the partial pressure of silicon precursor in the reactor;

- 10 comparing the calculated partial pressure of silicon precursor with a target partial pressure of silicon precursor; and

determining that the calculated partial pressure is less than the target partial pressure of silicon precursor;

- 15 and step (e) further comprises increasing the pressure in the reactor such that the partial pressure of silicon precursor is increased to at least the target partial pressure of silicon precursor.

As used herein, "calculated partial pressure of silicon precursor in the reactor" is equal to [the pressure in the reactor $\times$ the mole fraction of silicon precursor in the effluent gas withdrawn from the at least one gas outlet].

- 20 The target partial pressure of silicon precursor may be at least 10 kPa, or at least 20 kPa, or at least 30 kPa, or at least 40 kPa, or at least 50 kPa.

- The target partial pressure of silicon precursor may be no more than 5000 kPa, or no more than 4000 kPa, or no more than 3000 kPa, or no more than 2000 kPa, or no more than 1600 kPa, or no more than 1500 kPa, or no more than 1200 kPa, or no more than 1000 kPa, or
25 no more than 900 kPa, or no more than 800 kPa, or no more than 700 kPa, or no more than 600 kPa, or no more than 500 kPa, or no more than 400 kPa, or no more than 300 kPa, or no more than 250 kPa, or no more than 200 kPa, or no more than 150 kPa.

The pressure in step (e) may be at least 10 % greater than the pressure in step (b), or at least 20 % greater, or at least 30 % greater, or at least 40 % greater, or at least 50 % greater,

or at least 60 % greater, or at least 70 % greater, or at least 80 % greater, or at least 90 % greater, or at least 95 % greater.

- The pressure in step (e) may be no more than 5000 % greater than the pressure in step (b), or no more than 4000 % greater, or no more than 3000 % greater, or no more than 2000 % greater, or no more than 1000 % greater, or no more than 900 % greater, or no more than 800 % greater, or no more than 700 % greater, or no more than 600 % greater, or no more than 500 % greater, or no more than 400 % greater, or no more than 300 % greater, or no more than 175 % greater, or no more than 150 % greater, or no more than 125 % greater, or no more than 100 % greater.
- 5
- 10 The process may comprise the steps of: discontinuing deposition of the silicon; and withdrawing the composite particles from the reactor. Discontinuing deposition of the silicon may comprise discontinuing the introduction of the silicon precursor gas into the reactor; and/or reducing the pressure in the reactor to less than 50 kPa, or less than 40 kPa, or less than 30 kPa, or less than 20 kPa, or less than 10 kPa, or less than 5 kPa, or less than 3
- 15 kPa, or less than 2 kPa, or less than 1 kPa.

The porous particles may be mechanically agitated during steps (b) to (e). As used herein, "mechanically agitated" refers to the use of mechanical energy to stir or mix the porous particles in the reactor. The mechanical energy may be provided by, for example, an agitator in the reactor, rotation of the reactor vessel or mechanical vibration. Suitable

20 reactors for mechanically agitating the porous particles include but are not limited to a stirred-tank reactor, a rotating tank reactor (such as a rotary kiln) and a vibratory fluidized bed. Other suitable reactors for mechanically agitating the porous particles include but are not limited to, a tumbling fluidised bed and a rolling-fluidised bed.

The porous particles may be moved through a reaction zone in the reactor during steps (b)

25 to (e). Suitable reactors include but are not limited to a moving bed reactor

The reactor may be a stirred-tank reactor. A stirred-tank reactor is particularly preferred when the pressure in the reactor is above atmospheric pressure. In one embodiment, the reactor is a stirred-tank reactor and the pressure in step (b) is at least 150 kPa, or at least 200 kPa, or at least 250 kPa, or at least 300 kPa, or at least 400 kPa, or at least 500 kPa,

30 or at least 600 kPa.

The reactor may be a pressure reactor.

The porous particles may be continuously mechanically agitated during steps (b) to (e).

The porous particles may be mechanically fluidised during steps (b) to (e). As used herein, “mechanically fluidised” refers to the use of mechanical energy to fluidise the porous particles. In principle, it is not excluded that the flow of silicon precursor gas contributes to the fluidization of the porous particles when they are mechanically fluidised.

Preferably the reactor comprises an agitator for agitating the porous particles during steps (b) to (e). Any suitable agitator may be used, such as a turbine agitator, a paddle agitator, an anchor agitator, a propeller agitator, or a helical agitator.

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

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

Mechanically fluidising the porous particles effectively breaks up agglomerates which form naturally due to the cohesive nature of the porous particles. Therefore, both heat and mass transfer challenges are addressed.

The temperature may be increased or decreased during steps (b) to (e). It is preferred that the range in the temperature during steps (b) to (e) is no more than 50 °C, or no more than

40 °C, or no more than 30 °C, or no more than 20 °C, or no more than 10 °C. As used herein, "range in the temperature during steps (b) to (e)" means the statistical range, i.e. the difference between the smallest and largest temperature throughout steps (b) to (e).

By controlling the range in temperature during steps (b) to (e) it is possible to reduce time losses incurred by temperature correction.

The temperature in the reactor during steps (b) to (e) is preferably maintained in the range from 340 to 500 °C, or from 350 to 500 °C, or from 350 to 480 °C, or from 350 to 450 °C, or from 350 to 420 °C, or from 340 to 400 °C, or from 340 to 395 °C, or from 340 to 390 °C, or from 345 to 400 °C, or from 345 to 395 °C, or from 345 to 390 °C, or from 350 to 400 °C, or from 350 to 395 °C, or from 350 to 390 °C, or from 350 to 385 °C, or from 350 to 380 °C, or from 355 to 400 °C, or from 355 to 395 °C, or from 355 to 390 °C, or from 355 to 385 °C, or from 355 to 380 °C, or from 360 to 400 °C, or from 360 to 395 °C, or from 360 to 390 °C, or from 360 to 385 °C, or from 360 to 380 °C, or from 365 to 400 °C, or from 365 to 395 °C, or from 365 to 390 °C, or from 365 to 385 °C, or from 365 to 380 °C, or from 370 to 400 °C, or from 370 to 395 °C, or from 370 to 390 °C, or from 370 to 385 °C, or from 375 to 385 °C. Operation at greater temperatures in the reactor will increase the rate of the reaction and lead to faster deposition rate. The temperature in the reactor during steps (b) to (e) may be at least 340 °C, or at least 350 °C, or at least 355 °C, or at least 360 °C, or at least 365 °C, or at least 370 °C, or at least 375 °C. The temperature in the reactor during step (b) may be no more than 500 °C, or no more than 480 °C, or no more than 450 °C, or no more than 420 °C, or no more than 400 °C, or no more than 395 °C, or no more than 390 °C, or no more than 385 °C.

The process of the invention is preferably operated under a regime where the silicon 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 silicon precursor into the pore network of the porous particles, the reaction temperature in the reactor is preferably no more than 420 °C, more preferably no more than 410 °C, more preferably no more than 400 °C, more preferably no more than 395 °C. A temperature range of from 370 to 395 °C is particularly preferred.

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

The pressure in step (b) and/or step (e) may be below atmospheric pressure (about 101 kPa), at atmospheric pressure, or above atmospheric pressure. It is preferred that the pressure in at least step (e) is above atmospheric pressure.

The pressure in step (b) and/or step (e) may be at least 50 kPa.

- 5 The pressure in step (b) and/or step (e) may be less than atmospheric pressure, or no more than 100 kPa, or no more than 95 kPa, or no more than 90 kPa, or no more than 85 kPa, or no more than 80 kPa, or no more than 75 kPa.

- The pressure in step (b) and/or step (e) may be at least atmospheric pressure (about 101 kPa), or at least 105 kPa, or at least 110 kPa, or at least 115 kPa, or at least 120 kPa, or at
10 least 150 kPa, or at least 200 kPa, or at least 250 kPa, or at least 300 kPa, or at least 400 kPa, or at least 500 kPa, or at least 600 kPa.

The pressure in step (b) and/or step (e) may be at least 200 kPa, or at least 250 kPa, or at least 300 kPa, or at least 400 kPa, or at least 500 kPa, or at least 600 kPa.

- The pressure in step (b) and/or step (e) may be no more than 5000 kPa, or no more than
15 4000 kPa, or no more than 3000 kPa, or no more than 2000 kPa, or no more than 1600 kPa, or no more than 1500 kPa, or no more than 1200 kPa, or no more than 1000 kPa, or no more than 900 kPa, or no more than 800 kPa.

- The pressure in step (b) and/or step (e) may be in the range from 105 to 5000 kPa, or from 110 to 4000 kPa, or from 115 to 3000 kPa, or from 120 to 2000 kPa, or from 150 to 2000
20 kPa, or from 200 to 2000 kPa.

The pressure in step (b) and/or step (e) may be in the range from 200 to 5000 kPa, or from 200 to 4000 kPa, or from 200 to 3000 kPa, or from 200 to 2000 kPa, or from 200 to 1600 kPa, or from 200 to 1500 kPa.

- The pressure in step (b) and/or step (e) may be in the range from 250 to 1600 kPa, or from
25 300 to 1500 kPa, or from 400 to 1200 kPa, or from 500 to 1000 kPa, or from 500 to 900 kPa, or from 600 to 800 kPa.

Preferably, the pressure in step (b) and/or step (e) is in the range from 200 to 2000 kPa, or from 600 to 800 kPa.

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

To prevent uncontrolled reaction, the temperature in the reactor is preferably reduced as the pressure is increased. In particular, where the pressure in the reactor is above atmospheric pressure, 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 steps (b) to (e) is in the range from 340 to 500 °C and the pressure in the reactor during steps (b) to (e) is in the range from 105 to 5000 kPa.

Preferably, the temperature in the reactor during steps (b) to (e) is in the range from 360 to 390 °C and the pressure in the reactor during steps (b) to (e) is in the range from 110 to 4000 kPa.

Preferably, the temperature in the reactor during steps (b) to (e) is in the range from 365 to 390 °C and the pressure in the reactor during steps (b) to (e) is in the range from 115 to 3000 kPa.

Preferably, the temperature in the reactor during steps (b) to (e) is in the range from 375 to 385 °C and the pressure in the reactor during steps (b) to (e) is in the range from 200 to 2000 kPa.

The flow rate of the silicon precursor gas into the reactor may be increased or decreased during steps (b) to (e). It is preferred that the flow rate of the silicon precursor gas into the reactor is maintained during steps (b) to (e). As used herein, maintaining the flow rate of the silicon precursor gas into the reactor means the percent deviation in the flow rate of the silicon precursor gas into the reactor during steps (b) to (e) is no more than 20 %.

Maintaining the flow rate of the silicon precursor gas into the reactor within a small degree of variation improves the ability to control the conditions in the reactor through adjusting the at least one gas outlet of the reactor.

The percent deviation in the flow rate of the silicon precursor gas into the reactor is no more than 18 %, or no more than 15 %, or no more than 10 %, or no more than 5 %, or no more than 3 %, or no more than 2 %, or no more than 1 %.

As described herein, the present invention is particularly suitable for scale-up and producing large quantities of material. Thus, preferred embodiments of the invention involve high porous particle loading of the reactor, which can achieve high throughput and reduce synthesis times and costs. Synthesis time is reduced via high porous particle loading due to the minimisation of inter-batch operations such as porous particle loading, heating of the reactor and preparing an inert atmosphere. Reducing the number of batches whilst maintaining production throughput then results in a lower overall time. Porous particle loading of the reactor may be defined herein in terms of: porous particle volumes per litre of reactor, ratios of the internal surface area of the reactor to mass of porous particles in the reactor, and/or bed depths of the porous particles in the reactor.

The plurality of porous particles in the reactor in step (a) may be a charge of porous particles having a volume of at least 20 cm³ per litre of reactor volume (cm³/L_{RV}), or at least 50 cm³/L_{RV}, or at least 80 cm³/L_{RV}, or at least 100 cm³/L_{RV}, or at least 150 cm³/L_{RV}, or at least 200 cm³/L_{RV}, or at least 250 cm³/L_{RV}, or at least 300 cm³/L_{RV}, or at least 400 cm³/L_{RV}, or at least 500 cm³/L_{RV}, or at least 600 cm³/L_{RV}, or at least 700 cm³/L_{RV}, or at least 800 cm³/L_{RV}, or at least 900 cm³/L_{RV}.

Preferably, the charge of porous particles used in step (a) is at least 500 cm³/L_{RV} and in some embodiments is optionally sufficient so as to substantially fill the reactor volume of the reactor.

As used herein, the volume of the porous particles refers to the equivalent mass of the porous particles as determined from the tap density. For example, a particle volume of 200 cm³ of a porous particle material having a tap density of 1000g/L as defined herein is equivalent to 200 g of the porous particle material.

The ratio of the internal surface area of the reactor to mass of porous particles in the reactor may be no more than 1 m²/kg, or no more than 0.9 m²/kg, or no more than 0.8 m²/kg, or no

more than 0.7 m²/kg, or no more than 0.6 m²/kg, or no more than 0.5 m²/kg, or no more than 0.4 m²/kg, or no more than 0.3 m²/kg.

The ratio of the internal surface area of the reactor to mass of porous particles in the reactor may be at least 0.001 m²/kg, or at least 0.002 m²/kg, or at least 0.003 m²/kg, or at least
5 0.004 m²/kg, or at least 0.006 m²/kg, or at least 0.008 m²/kg, or at least 0.01 m²/kg.

The bed depth of the porous particles in the reactor may be at least 11 cm, or at least 15 cm, or at least 20 cm, or at least 25 cm, or at least 30 cm.

It is preferred to combine the aforementioned porous particle volumes per litre of reactor, ratios of the internal surface area of the reactor to mass of porous particles in the reactor, and/or bed depths of the porous particles in the reactor with continuous agitation as
10 described herein.

The plurality of porous particles in the reactor in step (a) may have a volume of at least 100 cm³/L_{RV} and the bed depth of the porous particles in the reactor may be at least 11 cm.

The plurality of porous particles in the reactor in step (a) may have a volume of at least 200
15 cm³/L_{RV} and the bed depth of the porous particles in the reactor may be at least 15 cm.

The plurality of porous particles in the reactor in step (a) may have a volume of at least 300 cm³/L_{RV} and the bed depth of the porous particles in the reactor may be at least 20 cm.

The plurality of porous particles in the reactor in step (a) may have a volume of at least 400 cm³/L_{RV} and the bed depth of the porous particles in the reactor may be at least 25 cm.

20 The plurality of porous particles in the reactor in step (a) may have a volume of at least 500 cm³/L_{RV} and the bed depth of the porous particles in the reactor may be at least 30 cm.

The plurality of porous particles in the reactor in step (a) may have a volume of at least 100 cm³/L_{RV} and the ratio of the internal surface area of the reactor to mass of porous particles in the reactor may be no more than 1 m²/kg.

25 The plurality of porous particles in the reactor in step (a) may have a volume of at least 200 cm³/L_{RV} and the ratio of the internal surface area of the reactor to mass of porous particles in the reactor may be no more than 0.9 m²/kg.

The plurality of porous particles in the reactor in step (a) may have a volume of at least 300 $\text{cm}^3/\text{L}_{\text{RV}}$ and the ratio of the internal surface area of the reactor to mass of porous particles in the reactor may be no more than 0.8 m^2/kg .

- 5 The plurality of porous particles in the reactor in step (a) may have a volume of at least 400 $\text{cm}^3/\text{L}_{\text{RV}}$ and the ratio of the internal surface area of the reactor to mass of porous particles in the reactor may be no more than 0.7 m^2/kg .

The plurality of porous particles in the reactor in step (a) may have a volume of at least 500 $\text{cm}^3/\text{L}_{\text{RV}}$ and the ratio of the internal surface area of the reactor to mass of porous particles in the reactor may be no more than 0.6 m^2/kg .

- 10 The plurality of porous particles in the reactor in step (a) may have a volume of at least 600 $\text{cm}^3/\text{L}_{\text{RV}}$ and the ratio of the internal surface area of the reactor to mass of porous particles in the reactor may be no more than 0.5 m^2/kg .

- Particularly preferred embodiments of the invention combine high porous particle loading of the reactor with a relatively low flow rate of the silicon precursor gas into the reactor. Flow rate of the silicon precursor gas into the reactor may be defined herein in terms of: grams of silicon in the silicon precursor per minute per kilogram of porous particles ($\text{gmin}^{-1}\text{kg}^{-1}$) and/or grams of silicon in the silicon precursor per minute per litre of reactor volume ($\text{gmin}^{-1}/\text{L}_{\text{RV}}$). The combination of high porous particle loading of the reactor with a relatively low flow rate of the silicon precursor gas into the reactor allows for a better control of the quality of the material, even when producing large quantities of material. As the flow rate of the silicon precursor gas increases, the temperature of the reactor during the deposition reaction must be increased, which results in poor infiltration of the silicon precursor within the porous network of the particles. It is believed that poor infiltration of the silicon precursor within the porous network of the particles can increase the amount of coarse silicon to undesirable levels, which is detrimental to product quality. It is believed that this is because at high temperature regimes the kinetics of the deposition reaction prevail over mass transfer, resulting in poor infiltration of the silicon precursor within the porous network of the particles.

- 30 The flow rate of the silicon precursor gas into the reactor in grams of silicon in the silicon precursor per minute per kilogram of porous particles may be from 0.2 to 25 $\text{gmin}^{-1}\text{kg}^{-1}$, or from 0.5 to 20 $\text{gmin}^{-1}\text{kg}^{-1}$, or from 1 to 15 $\text{gmin}^{-1}\text{kg}^{-1}$, or from 1 to 14 $\text{gmin}^{-1}\text{kg}^{-1}$, or from 1 to

13 $\text{gmin}^{-1}\text{kg}^{-1}$, or from 1 to 12 $\text{gmin}^{-1}\text{kg}^{-1}$, or from 2 to 12 $\text{gmin}^{-1}\text{kg}^{-1}$, or from 3 to 12 $\text{gmin}^{-1}\text{kg}^{-1}$, or from 3 to 11 $\text{gmin}^{-1}\text{kg}^{-1}$. This is the flow rate during steps (b) to (e).

It is preferred that the flow rate of the silicon precursor gas into the reactor during steps (b) to (e) in grams of silicon in the silicon precursor per minute per kilogram of porous particles
5 is from 0.2 to 5 $\text{gmin}^{-1}\text{kg}^{-1}$, or from 0.2 to 4 $\text{gmin}^{-1}\text{kg}^{-1}$, or from 0.2 to 3 $\text{gmin}^{-1}\text{kg}^{-1}$.

The flow rate of the silicon precursor gas into the reactor during steps (b) to (e) in grams of silicon in the silicon precursor per minute per litre of reactor volume ($\text{gmin}^{-1}/\text{L}_{\text{RV}}$) may be from 0.03 to 40 $\text{gmin}^{-1}/\text{L}_{\text{RV}}$, or from 0.04 to 35 $\text{gmin}^{-1}/\text{L}_{\text{RV}}$, or from 0.05 to 30 $\text{gmin}^{-1}/\text{L}_{\text{RV}}$, or from 0.06 to 25 $\text{gmin}^{-1}/\text{L}_{\text{RV}}$, or from 0.07 to 20 $\text{gmin}^{-1}/\text{L}_{\text{RV}}$, or from 0.08 to 15 $\text{gmin}^{-1}/\text{L}_{\text{RV}}$, or
10 from 0.09 to 10 $\text{gmin}^{-1}/\text{L}_{\text{RV}}$, or from 0.1 to 5 $\text{gmin}^{-1}/\text{L}_{\text{RV}}$, or from 0.1 to 1 $\text{gmin}^{-1}/\text{L}_{\text{RV}}$, or from 0.15 to 1 $\text{gmin}^{-1}/\text{L}_{\text{RV}}$, or from 0.15 to 0.95 $\text{gmin}^{-1}/\text{L}_{\text{RV}}$, or from 0.2 to 0.95 $\text{gmin}^{-1}/\text{L}_{\text{RV}}$, or from 0.2 to 0.9 $\text{gmin}^{-1}/\text{L}_{\text{RV}}$.

It is preferred that the flow rate of the silicon precursor gas into the reactor during steps (b) to (e) in grams of silicon in the silicon precursor per minute per litre of reactor volume is
15 from 0.03 to 0.55 $\text{gmin}^{-1}/\text{L}_{\text{RV}}$, or from 0.03 to 0.45 $\text{gmin}^{-1}/\text{L}_{\text{RV}}$, or from 0.03 to 0.35 $\text{gmin}^{-1}/\text{L}_{\text{RV}}$.

Control over the flow rate of the effluent gas may be achieved using Coriolis flow meters and controllers, or other mass flow controllers where the mass flow rate is measured and used to control the gas flow rate. Suitable valves for controlling flow rate include but are not limited to needle valves, diaphragm valves and glove valves.

20 Particularly preferred embodiments of the invention combine high porous particle loading of the reactor with a relatively low flow rate of the silicon precursor gas into the reactor.

The plurality of porous particles in the reactor in step (a) may have a volume of at least 100 $\text{cm}^3/\text{L}_{\text{RV}}$ and the bed depth of the porous particles in the reactor may be at least 11 cm and the flow rate of the silicon precursor gas into the reactor during steps (b) to (e) may be from
25 0.2 to 5 $\text{gmin}^{-1}\text{kg}^{-1}$.

The plurality of porous particles in the reactor in step (a) may have a volume of at least 200 $\text{cm}^3/\text{L}_{\text{RV}}$ and the bed depth of the porous particles in the reactor may be at least 15 cm and the flow rate of the silicon precursor gas into the reactor during steps (b) to (e) may be from 0.2 to 4 $\text{gmin}^{-1}\text{kg}^{-1}$.

The plurality of porous particles in the reactor in step (a) may have a volume of at least 300 cm³/L_{RV} and the bed depth of the porous particles in the reactor may be at least 20 cm and the flow rate of the silicon precursor gas into the reactor during steps (b) to (e) may be from 0.2 to 3 gmin⁻¹kg⁻¹.

- 5 The plurality of porous particles in the reactor in step (a) may have a volume of at least 400 cm³/L_{RV} and the bed depth of the porous particles in the reactor may be at least 25 cm and the flow rate of the silicon precursor gas into the reactor during steps (b) to (e) may be from 0.2 to 3 gmin⁻¹kg⁻¹.

- 10 The plurality of porous particles in the reactor in step (a) may have a volume of at least 500 cm³/L_{RV} and the bed depth of the porous particles in the reactor may be at least 30 cm and the flow rate of the silicon precursor gas into the reactor during steps (b) to (e) may be from 0.2 to 3 gmin⁻¹kg⁻¹.

- 15 The plurality of porous particles in the reactor in step (a) may have a volume of at least 100 cm³/L_{RV} and the ratio of the internal surface area of the reactor to mass of porous particles in the reactor may be no more than 1 m²/kg and the flow rate of the silicon precursor gas into the reactor during steps (b) to (e) may be from 0.2 to 5 gmin⁻¹kg⁻¹.

- 20 The plurality of porous particles in the reactor in step (a) may have a volume of at least 200 cm³/L_{RV} and the ratio of the internal surface area of the reactor to mass of porous particles in the reactor may be no more than 0.9 m²/kg and the flow rate of the silicon precursor gas into the reactor during steps (b) to (e) may be from 0.2 to 4 gmin⁻¹kg⁻¹.

The plurality of porous particles in the reactor in step (a) may have a volume of at least 300 cm³/L_{RV} and the ratio of the internal surface area of the reactor to mass of porous particles in the reactor may be no more than 0.8 m²/kg and the flow rate of the silicon precursor gas into the reactor during steps (b) to (e) may be from 0.2 to 3 gmin⁻¹kg⁻¹.

- 25 The plurality of porous particles in the reactor in step (a) may have a volume of at least 400 cm³/L_{RV} and the ratio of the internal surface area of the reactor to mass of porous particles in the reactor may be no more than 0.7 m²/kg and the flow rate of the silicon precursor gas into the reactor during steps (b) to (e) may be from 0.2 to 3 gmin⁻¹kg⁻¹.

- 30 The plurality of porous particles in the reactor in step (a) may have a volume of at least 500 cm³/L_{RV} and the ratio of the internal surface area of the reactor to mass of porous particles

in the reactor may be no more than $0.6 \text{ m}^2/\text{kg}$ and the flow rate of the silicon precursor gas into the reactor during steps (b) to (e) may be from 0.2 to $3 \text{ gmin}^{-1}\text{kg}^{-1}$.

The plurality of porous particles in the reactor in step (a) may have a volume of at least $600 \text{ cm}^3/\text{L}_{\text{RV}}$ and the ratio of the internal surface area of the reactor to mass of porous particles
5 in the reactor may be no more than $0.5 \text{ m}^2/\text{kg}$ and the flow rate of the silicon precursor gas into the reactor during steps (b) to (e) may be from 0.2 to $3 \text{ gmin}^{-1}\text{kg}^{-1}$.

The composite particles may comprise a target silicon content and 5 to 95 % of the target silicon content may be deposited in step (b). As used herein, "target silicon content" means the amount of silicon in the composite particles prepared according to the process of the
10 invention.

The target silicon content may be an amount of silicon that occupies from 20% to 95% of the internal pore volume of the porous particle framework. The target silicon content may occupy from 20% to 80%, or from 20% to 70%, or from 30% to 70%, or from 30% to 60% of the internal pore volume of the porous particle framework.

15 The target silicon content may be 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.

The target silicon content may be no more than 70 wt% silicon, or no more than 65 wt%
20 silicon, or 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.

At least 10 % of the target silicon content may be deposited in step (b), or at least 15 %, or at least 20 %, or at least 25 %, or at least 30 %, or at least 35 %, or at least 40 %, or at least 45 %, or at least 50 %, or at least 55 %, or at least 60 %, or at least 65 %, or at least 70 %, or at least 75 %, or at least 80 %, or at least 85 %, or at least 90 %.
25

No more than 90 % of the target silicon content may be deposited step (b), or no more than 85 %, or no more than 80 %, or no more than 75 %, or no more than 70 %, or no more than 65 %, or no more than 60 %, or no more than 55 %, or no more than 50 %, or not more than 45 %, or no more than 40 %, or no more than 35 %, or no more than 30 %, or no more than 25 %, or no more than 20 %, or no more than 15 %, or no more than 10 %.
30

The composite particles produced by a process according to the invention may comprise from 0.2 to 1.8 grams of silicon per gram of the porous particle framework.

The composite particles produced by a process according to the invention may comprise an amount of silicon that occupies from 20% to 95% of the internal pore volume of the porous particle framework, or from 20% to 80%, or from 20% to 70%, or from 30% to 70%,
5 or from 30% to 60% of the internal pore volume of the porous particle framework. Silicon occupancy may be calculated using the equation $100 \times (\text{density of silicon} \times \text{weight \% of silicon in the composite particle}) / \text{pore volume of porous particle}$. The density of silicon is assumed to be 2.3 g/cm³ for this purpose.

10 It is not excluded that unreacted silicon precursor may be recovered from the effluent gas withdrawn from the reactor and recycled into the reactor.

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

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

Optionally, the plurality of porous particles is pre-heated before it is introduced into the reactor. Preferably, the plurality of porous particles is pre-heated to a temperature that is $\geq (T_{RZ} - 200) ^\circ\text{C}$, wherein T_{RZ} is the reaction temperature of the reactor in step (b), preferably
25 to a temperature that is $\geq (T_{RZ} - 100) ^\circ\text{C}$, more preferably to a temperature that is $\geq (T_{RZ} - 50) ^\circ\text{C}$.

Optionally, the silicon precursor gas is pre-heated before it is introduced into the reactor. Preferably, the silicon precursor gas is pre-heated to a temperature that is $\geq (T_{RZ} - 200) ^\circ\text{C}$, wherein T_{RZ} is the reaction temperature of the reactor, preferably to a temperature that is
30 $\geq (T_{RZ} - 100) ^\circ\text{C}$, more preferably to a temperature that is $\geq (T_{RZ} - 50) ^\circ\text{C}$.

The composite particles produced by the process according to the invention preferably have a BET surface area of no more than 100 m²/g, or no more than 80 m²/g, or no more than 60 m²/g, or no more than 40 m²/g, or no more than 30 m²/g, or no more than 25 m²/g, or no more than 20 m²/g, or no more than 15 m²/g, or no more than 10 m²/g. In general, a low
5 BET surface area is preferred in order to minimize the formation of solid electrolyte interphase (SEI) layers at the surface of the composite particles during the first charge-discharge cycle of an anode. However, a 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
10 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
15 from a measurement of the physical adsorption of gas molecules on a solid surface, using the Brunauer–Emmett–Teller theory, in accordance with ISO 9277 (2022).

The 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
20 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
25 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:

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

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
30 between 550 °C to 650 °C, $M_{\min}$ is the minimum mass of the sample above 150 °C and below 500 °C, and M_i 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 provided by the process according to the invention 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.

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

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

Wherein Z is the percentage of unoxidized silicon at 800 °C, M₈₀₀ 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 SiO₂ and that the total mass at completion of oxidation is SiO₂. Typically, the TGA analysis is carried out using a sample size of 10 mg ± 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.

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

and no more than 5 wt% of the silicon is coarse bulk silicon, wherein both are determined by TGA. More preferably, at least 45 wt% of the silicon is surface silicon and no more than 2 wt% of the silicon is coarse bulk silicon, wherein both are determined by TGA.

POROUS PARTICLES

- 5 The porous particles may comprise micropores and/or mesopores.

The porous particles may 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
10 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
15 " D_{50} " and " D_{50} particle diameter" as used herein refer to the volume-based median particle diameter, i.e. the diameter below which 50% by volume of the particle population is found. The terms " D_{10} " and " D_{10} particle diameter" as used herein refer to the 10th percentile volume-based median particle diameter, i.e. the diameter below which 10% by volume of the particle population is found. The terms " D_{90} " and " D_{90} particle diameter" as used herein
20 refer to the 90th percentile volume-based median particle diameter, i.e. the diameter below which 90% by volume of the particle population is found.

Particle diameters and particle size distributions can be determined by standard laser diffraction techniques in accordance with ISO 13320:2009. Laser diffraction relies on the principle that a particle will scatter light at an angle that varies depending on the size the
25 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™
30 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.

5 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 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.

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

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

The D_{10} particle diameter of the porous particles is preferably at least 0.2 μm , or at least 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 D_{10} particle diameter at 0.2 μm or more, the potential for undesirable
30 agglomeration of sub-micron sized particles is reduced, and improved dispersibility of the composite particles formed.

The D_{90} particle diameter of the porous particles is preferably no more than 300 μm , or no more than 250 μm , or no 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 .

- 5 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.
- 10 Preferably, the D_1 particle diameter of the porous particles is at least 0.8 μm , or at least 1.0 μm , or at least 1.2 μm , or at least 1.4 μm , or at least 1.5 μm , or at least 1.6 μm , or at least 1.8 μm , or at least 2.0 μm , or at least 2.2 μm , or at least 2.4 μm , or at least 2.5 μm , or at least 2.6 μm , or at least 2.8 μm , or at least 3.0 μm . It will be appreciated that the D_1 particle diameter of the porous particles provides a measure of the content of fine particles
- 15 in the charge of porous particles. It has been found that substantially eliminating fines from the porous particles provides for improved deposition of silicon, in particular by increasing the content of "surface silicon" in the composite particles. The "surface silicon" content of the composite particles is discussed in further detail below.

- 20 Preferably, the D_1 particle diameter is in the range from 1.5 to 4.5 μm , or from 2 to 4 μm , or from 2.5 to 3.5 μm , or from 11 to 13 μm .

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

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

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

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

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

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:

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

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.

The porous particles comprise a three-dimensionally interconnected open pore network comprising micropores and/or mesopores and optionally a minor volume of macropores. In accordance with conventional IUPAC terminology, the term "micropore" is used herein to refer to pores of less than 2 nm in diameter, the term "mesopore" is used 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 silicon into the pore volume in step (c).

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, at least 0.85 cm³/g, or at least 0.9 cm³/g, or at least 0.95 cm³/g, or at least 1 cm³/g. The use of high porosity conductive particles may be advantageous since it allows a larger amount of silicon to be accommodated within the pore structure.

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

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

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

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

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

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

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

The volumetric ratio of micropores to mesopores in the porous particles may range in principle from 100:0 to 0:100. 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 micropore volume fraction is preferably at least 0.4, or at least 0.45, or at least 0.5, or
25 at least 0.55, or at least 0.6, based on the total volume of micropores and mesopores in the porous particles.

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

- For example, the micropore volume fraction may be in the range from 0.4 to 0.85, or in the
30 range from 0.45 to 0.85, or in the range from 0.5 to 0.8, or in the range from 0.55 to 0.8, or in the range from 0.6 to 0.8, based on the total volume of micropores and mesopores in the

porous particles. Alternatively, the micropore volume fraction may be greater than 0.8, or greater than 0.85, or greater than 0.9, or greater than 0.95, or greater than 0.98, based on the total volume of micropores and mesopores in the porous particles.

5 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 bimodal or multimodal pore size distribution may be preferred since close proximity between micropores and pores of larger diameter provides the advantage of efficient ionic transport through the porous network to the silicon.

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

25 Nitrogen gas adsorption is effective for the measurement of pore volume and pore size distributions for pores having a diameter up to 50 nm, but is less reliable for pores of much larger diameter. For the purposes of the present invention, nitrogen adsorption is therefore used to determine pore volumes and pore size distributions only for pores having a diameter up to and including 50 nm (i.e. only for micropores and mesopores). PD_{50} are likewise
30 determined relative to the total volume of micropores and mesopores only.

In view of the limitations of available analytical techniques it is not possible to measure pore volumes and pore size distributions across the entire range of micropores, mesopores and

macropores using a single technique. In the case that the porous particles comprise macropores, the volume of pores having diameter in the range from greater than 50 nm and up to 100 nm may be measured by mercury porosimetry and is preferably no more than 0.3 cm³/g, or no more than 0.20 cm³/g, or no more than 0.1 cm³/g, or no more than 0.05 cm³/g. A small fraction of macropores may be useful to facilitate electrolyte access into the pore network, but the advantages of the invention are obtained substantially by accommodating silicon in micropores and smaller mesopores.

Any pore volume measured by mercury porosimetry at pore sizes of 50 nm or below is disregarded (as set out above, nitrogen adsorption is used to characterize the mesopores and micropores). Pore volume measured by mercury porosimetry above 100 nm is assumed for the purposes of the invention to be inter-particle porosity and is also disregarded.

Mercury porosimetry is a technique that characterizes the porosity and pore diameter distributions of a material by applying varying levels of pressure to a sample of the material immersed in mercury. The pressure required to intrude mercury into the pores of the sample is inversely proportional to the size of the pores. Values obtained by mercury porosimetry as reported herein are obtained in accordance with ASTM UOP578-11, with the surface tension γ taken to be 480 mN/m and the contact angle ϕ taken to be 140° for mercury at room temperature. The density of mercury is taken to be 13.5462 g/cm³ at room temperature. A number of high precision mercury porosimetry instruments are commercially available, such as the AutoPore IV series of automated mercury porosimeters available from Micromeritics Instrument Corporation, USA. For a complete review of mercury porosimetry reference may be made to P.A. Webb and C. Orr in "Analytical Methods in Fine Particle Technology, 1997, Micromeritics Instrument Corporation, ISBN 0-9656783-0.

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

pores that are so small as to be below the limit of detection by nitrogen adsorption is not taken into account.

The porous particles are preferably porous conductive particles. A preferred type of porous conductive particles is porous carbon particles. The porous carbon particles preferably
5 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.

10 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
15 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). The porous carbon particles may comprise an ID/IG of no more than 0.84, or no more than 0.75.

20 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
25 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.

30 Examples of organic materials that may be used include plant biomass including lignocellulosic materials (such as coconut shells, rice husks, wood etc.) and fossil carbon sources such as coal. Examples of resins and polymeric materials which form porous

carbon particles on pyrolysis include phenolic resins, novolac resins, pitch, melamines, polyacrylates, polystyrenes, polyvinylalcohol (PVA), polyvinylpyrrolidone (PVP), and various copolymers comprising monomer units of acrylates, styrenes, α -olefins, vinyl pyrrolidone and other ethylenically unsaturated monomers. A variety of different carbon materials are available in the art depending on the starting material and the conditions of the pyrolysis process. Porous carbon particles of various different specifications are available from commercial suppliers.

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

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

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

The porous particles preferably have a BET surface area of at least 750 m²/g, or at least 1,000 m²/g, or at least 1,250 m²/g, or at least 1,500 m²/g. 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.

The porous particles preferably have a particle density of at least 0.35 and preferably less than 3 g/cm³, more preferably less than 2 g/cm³, more preferably less than 1.5 g/cm³, most preferably from 0.35 to 1.2 g/cm³. As used herein, the term "particle density" refers to "apparent particle density" as measured by mercury porosimetry (i.e. the mass of a particle divided by the particle volume wherein the particle volume is taken to be the sum of the

volume of solid material and any closed or blind pores (a "blind pore" is pore that is too small to be measured by mercury porosimetry)). In general, the particulate additives used in the present invention have a low BET surface area and thus a relatively low volume of open pores. Accordingly, the apparent density as measured by mercury porosimetry is a close
5 approximation to the "effective particle density" (the calculation of which includes the volume of open pores). Preferably, the porous particles have particle density of at least 0.4 g/cm³, or at least 0.45 g/cm³, or at least 0.5 g/cm³, or at least 0.55 g/cm³, or at least 0.6 g/cm³, or at least 0.65 g/cm³, or at least 0.7 g/cm³. Preferably, the porous particles have particle density of no more than 1.15 g/cm³, or no more than 1.1 g/cm³, or no more than 1.05 g/cm³,
10 or no more than 1 g/cm³, or no more than 0.95 g/cm³, or no more than 0.9 g/cm³.

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

- (i) the D₅₀ particle diameter is in the range from 0.5 to 30 µm;
- (ii) the total pore volume of micropores and mesopores as measured by gas adsorption is in the range from 0.5 to 1.5 cm³/g;
- 15 (iii) the PD₅₀ pore diameter as measured by gas adsorption is no more than 5 nm;

SILICON PRECURSOR GAS

The silicon precursor gas comprises a silicon precursor. A silicon precursor is a silicon compound or mixture of silicon compounds that is gaseous at the temperature of the CVD
20 process and thermally decomposable to form elemental silicon and by-product gases. The silicon precursor gas optionally includes other gases, such as an inert gas. Examples of suitable silicon precursors include silane (SiH₄), disilane (Si₂H₆), trisilane (Si₃H₈), methylsilane, dimethylsilane and chlorosilanes, and mixtures thereof. Preferably, the silicon precursor is selected from silane (SiH₄), disilane (Si₂H₆), trisilane (Si₃H₈), methylsilane and
25 dimethylsilane. Silane (SiH₄) is the most preferred silicon precursor.

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

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

The concentration of silicon precursor in the silicon precursor gas introduced into the reactor may be increased or decreased during steps (b) to (e). It is preferred that the range in concentration of silicon precursor in the silicon precursor gas introduced into the reactor during steps (b) to (e) is no more than 20 vol%, or no more than 10 vol%, or no more than 5 vol%, or no more than 3 vol%, or no more than 2 vol%, or no more than 1 vol%. As used
5 herein, "range in concentration of silicon precursor in the silicon precursor gas introduced into the reactor during steps (b) to (e)" means the statistical range, i.e. the difference between the smallest and largest concentration throughout steps (b) to (e).

The silicon precursor gas may comprise at least 10 vol%, or at least 20 vol%, or at least 30
10 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%, or 100 vol% of the silicon precursor. Preferably, the silicon precursor gas comprises at least 50 vol%, or at least 60 vol%, or at
15 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%, or 100 vol% of the silicon precursor. The vol% of silicon precursor refers to the concentration of silicon precursor as a proportion of the total gas (the silicon precursor gas) being introduced to the reactor.

Preferably, the range in concentration of silicon precursor in the silicon precursor gas
20 introduced into the reactor during steps (b) to (e) is no more than 20 vol% and the percent deviation in the flow rate of the silicon precursor gas into the reactor during steps (b) to (e) is no more than 20 %. In addition, the range in the temperature during steps (b) to (e) may be no more than 50 °C.

Preferably, the range in concentration of silicon precursor in the silicon precursor gas
25 introduced into the reactor during steps (b) to (e) is no more than 10 vol% and the percent deviation in the flow rate of the silicon precursor gas into the reactor during steps (b) to (e) is no more than 18 %. In addition, the range in the temperature during steps (b) to (e) may be no more than 40 °C.

Preferably, the range in concentration of silicon precursor in the silicon precursor gas
30 introduced into the reactor during steps (b) to (e) is no more than 10 vol% and the percent deviation in the flow rate of the silicon precursor gas into the reactor during steps (b) to (e)

is no more than 15 %. In addition, the range in the temperature during steps (b) to (e) may be no more than 30 °C.

Preferably, the range in concentration of silicon precursor in the silicon precursor gas introduced into the reactor during steps (b) to (e) is no more than 5 vol% and the percent
5 deviation in the flow rate of the silicon precursor gas into the reactor during steps (b) to (e) is no more than 10 %. In addition, the range in the temperature during steps (b) to (e) may be no more than 20 °C.

CARBON COATING

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

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
15 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
20 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,
25 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.

30 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.

20 PASSIVATION

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

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

- 30 Therefore, the process of the invention may further comprise the step of: contacting the composite particles with a passivating agent at conditions that are effective to passivate the composite particles. As defined herein, a passivating agent is a compound or mixture of compounds which is able to react with the surface of the deposited silicon to form a modified

surface. The composite particles may be contacted with a passivating agent in the reactor, or may be conveyed to a separate vessel for contacting with a passivating agent. The composite particles may be contacted with a first passivating agent in the reactor, subsequently conveyed to a separate vessel and contacted with a second passivating agent, wherein the first and second passivating agents may be the same or may be different. Preferably the composite particles are at least contacted with a passivating agent in the reactor.

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

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

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

The passivating agent may be an oxygen containing gas. In this case, conditions that are effective to passivate the composite particles may comprise a temperature in the range from 20 to 300 °C, or from 20 to 200 °C, or from 25 to 200 °C, or from 25 to 180 °C, or from 50 °C to 160 °C. Preferably, the temperature is no more than 150 °C. Further, conditions that are effective to passivate the composite particles may comprise a pressure in the range from 1 to 600 kPa, or from 10 to 500 kPa, or from 20 to 200 kPa, or from 50 to 150 kPa, or from 80 to 120 kPa, or about 100 kPa. The oxygen containing gas may be air. When the oxygen containing gas is air, the concentration of oxygen in contact with the composite particles during the passivation step may be increased over a period of time, optionally as the composite particles are cooled down to a temperature less than 50 °C.

The passivating agent may be ammonia or another nitrogen containing molecule. In this case, the passivation layer may comprise a silicon nitride of the formula SiN_x , wherein $0 <$

$x \leq 4/3$. The silicon nitride is preferably amorphous silicon nitride. A nitride layer may be formed by contacting the composite particles with ammonia at a temperature in the range from 200-700 °C, preferably from 400-700 °C, more preferably from 400-600 °C. The temperature may then be increased if necessary into the range of 500 to 1,000 °C to form a nitride surface (e.g. a silicon nitride surface of the formula SiN_x , wherein $x \leq 4/3$). As sub-stoichiometric nitrides (such as SiN_x , wherein $0 < x \leq 4/3$) are conductive, nitride interlayers function as a conductive network that allows for faster charging and discharging of the electroactive material.

Phosphine may also be used as a passivating agent, as a phosphorus analog of ammonia.

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

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

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

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

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

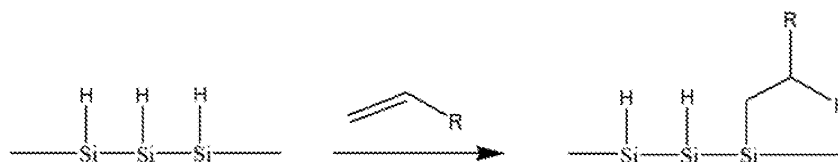
Particularly preferred passivating agents include one or more compounds of the formulae:

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

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

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

- 5 It is believed that passivating agents comprising an alkene, alkyne or carbonyl group undergo an insertion reaction with M-H groups at the surface of the electroactive material (where M represents an atom of the electroactive material) to form a covalently passivated surface which is resistant to oxidation by air. When silicon is the electroactive material, the passivation reaction between the silicon surface and the passivating agent may be understood as a form of hydrosilylation, as shown schematically below.
- 10



- Other suitable passivating agents include compounds including an active hydrogen atom bonded to oxygen, nitrogen, sulphur or phosphorus. For example, the passivating agent may be an alcohol, amine, thiol or phosphine. Reaction of the group $-XH$ with hydride groups at the surface of the electroactive material is understood to result in elimination of H_2 and the formation of a direct bond between X and the electroactive material surface.
- 15

Suitable passivating agents in this category include compounds of the formula

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

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

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

Preferably X represents O or NH.

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

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

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

GAS SEPARATION UNIT

The process may further comprise the steps of:

- 10 feeding at least a portion of the effluent gas to a gas separation unit; and
operating the gas separation unit to separate the silicon precursor from the at least one by-product gas.

- 15 Separating the silicon precursor and the at least one by-product gas provides at least one enriched gas stream and at least one waste gas stream, wherein the enriched gas stream is enriched in the silicon precursor compared to the effluent gas and wherein the waste gas stream is depleted in the silicon precursor compared to the effluent gas.

- The enriched gas stream may comprise the at least one by-product gas from the effluent gas, but it is preferred that the amount of the at least one by-product gas is minimised. For example, the enriched gas stream may comprise at least 60 vol% silicon precursor, or at
20 least 70 vol% silicon precursor, or at least 80 vol% silicon precursor, or at least 90 vol% silicon precursor, or at least 95 vol% silicon precursor, or at least 98 vol% silicon precursor. The waste gas stream may comprise silicon precursor, but it is preferred that the amount of silicon precursor is minimised. For example, the waste gas stream may comprise less than 40 vol% silicon precursor, or less than 30 vol% silicon precursor, or less than 20 vol% silicon
25 precursor, or less than 10 vol% silicon precursor, or less than 5 vol% silicon precursor.

- For example, CVD deposition of silane produces hydrogen gas as a by-product and unreacted silane can be separated from the silane/hydrogen mixture in the effluent gas using a gas separation unit to provide an enriched gas stream that is enriched in silane compared to the effluent gas and a waste gas stream comprising hydrogen and which is
30 depleted in silane compared to the effluent gas.

The enriched gas stream comprising silicon precursor may be recycled into the reactor, for example as part of step (b) thus minimising its make-up. Therefore, the process may comprise the step of:

introducing (recycling) at least a portion of the enriched gas stream into the reactor.

- 5 The enriched gas stream may be mixed with the silicon precursor gas introduced in step (b) and the mixture introduced into the reactor via the same gas inlet(s). Alternatively or in addition, the enriched gas stream may be introduced into the reactor via a different gas inlet(s) to the silicon precursor gas introduced in step (b). Alternatively or in addition, the enriched gas stream comprising silicon precursor may be stored. Similarly, the waste gas stream comprising by-product gases such as hydrogen may be stored.
- 10

- Step (b) may comprise combining at least a portion of the enriched gas stream with the silicon precursor gas before being introduced into the reactor. Alternatively or in addition, the process may further comprise the step of: introducing at least a portion of the enriched gas stream into the reactor separately from the silicon precursor gas. Alternatively or in addition, the process may further comprise the step of: collecting at least a portion of the enriched gas stream and/or waste gas stream for storage. Alternatively or in addition, at least a portion of the enriched gas stream may undergo further processes to purify the silicon precursor gas.
- 15

- At least a portion of the waste gas stream may undergo further processes to recover energy and/or purify the by-product gases. At least a portion of the waste gas stream may be purified. Alternatively or in addition, at least a portion of the waste gas stream may be processed to recover energy therefrom. Alternatively or in addition, at least a portion of the waste gas stream may be fed to a supply grid. Alternatively or in addition, at least a portion of the waste gas stream may be used as a feedstock in a further process.
- 20

- 25 A portion of the effluent gas may bypass the gas separation unit as a bypass stream. Therefore, the process may further comprise the step of: bypassing a portion of the effluent gas around the gas separation unit as a bypass stream. Step (b) may comprise combining at least a portion of the bypass stream with the silicon precursor gas before being introduced into the reactor. Alternatively or in addition, at least a portion of the bypass stream may be introduced into the reactor separately from the silicon precursor gas. The process may comprise separating a bypass stream from the effluent stream and recycling the bypass
- 30

stream into the reactor without separating the silicon precursor in the bypass stream from the by-product gas in the bypass stream

The effluent gas may comprise from 5 to 80 vol% of the silicon precursor, or from 5 to 70 vol%, or from 5 to 60 vol%, or from 5 to 50 vol% of the silicon precursor.

- 5 The by-product gas may comprise hydrogen and the gas separation unit may be a hydrogen (H₂)-selective membrane. The by-product gas may comprise hydrogen and the gas separation unit may be a hydrogen (H₂)-silane selective membrane.

- The effluent gas may comprise an inert gas, and the process may comprise the step of: using the gas separation unit to separate the inert gas and the silicon precursor and/or the
10 at least one by-product gas. The inert gas, the silicon precursor and the at least one by-product gas may be separated sequentially. For example, silicon precursor may be separated from the inert gas and the at least one by-product gas, then the at least one by-product gas may be separated from the inert gas. In this case, the gas separation unit may comprise two or more systems for separating the gases.

- 15 The gas separation unit may comprise a membrane separation system such as a polymeric membrane separation system and/or a metal alloy membrane separation system, a pressure swing adsorption system, a cryogenic separation system, a gas distillation system, or a combination thereof. The gas separation unit may comprise a membrane separation system and a pressure swing adsorption system.

- 20 The separation unit may comprise a heat exchanger to cool the effluent gas to ambient or near ambient temperature, such as less than 70 °C, or less than 50 °C, before the effluent gas is separated into an enriched gas stream and a waste gas stream. Therefore, the process may comprise the step of: cooling the effluent gas to ambient or near ambient temperature, such as less than 70 °C, or less than 50 °C.

25 FIGURES

The present invention is further described with reference to the appended figures, in which:

Figure 1 is a graphical representation of a process operated according to an embodiment of the invention.

Figure 2 is a graphical representation of a process operated according to an embodiment of the invention.

Figure 3 is a graphical representation of a process operated according to an embodiment of the invention.

- 5 Figure 4 is a graphical representation of a process operated according to an embodiment of the invention.

Figure 5 is a graphical representation of a process operated according to an embodiment of the invention.

- 10 Figure 6 is a graphical representation of a process operated according to an embodiment of the invention.

Figure 7 is a graphical representation of a process operated according to an embodiment of the invention.

Figure 8 is a graphical representation of a process operated according to an embodiment of the invention.

- 15 Figure 9 is a graphical representation of a process operated according to an embodiment of the invention.

Figure 10 is a graphical representation of a process operated according to an embodiment of the invention.

- 20 In Figures 1 and 2, silicon precursor is injected into the reactor at conditions effective to cause deposition of silicon in the pores of the porous particles and the pressure is increased to increase the calculated conversion of silicon precursor to a target conversion of silicon precursor. After 20 % of the target silicon content is deposited the calculated conversion of silicon precursor remains at the target conversion of silicon precursor. After 60 % of the target silicon content is deposited the calculated conversion of silicon precursor is less than
- 25 the target conversion of silicon precursor and the pressure in the reactor is increased to increase the calculated conversion of silicon precursor to a target conversion of silicon precursor. After 80 % of the target silicon content is deposited the calculated conversion of silicon precursor remains at the target conversion of silicon precursor. After 90 % of the target silicon content is deposited the calculated conversion of silicon precursor is less than

the target conversion of silicon precursor and the pressure in the reactor is increased to increase the calculated conversion of silicon precursor to a target conversion of silicon precursor until 100 % of the target silicon content is deposited.

5 In Figures 3 and 4, silicon precursor is injected into the reactor at conditions effective to cause deposition of silicon in the pores of the porous particles and the pressure is increased to increase the calculated conversion of silicon precursor to a target conversion of silicon precursor. After 5 % of the target silicon content is deposited the calculated conversion of silicon precursor remains at the target conversion of silicon precursor. After 60 % of the target silicon content is deposited the calculated conversion of silicon precursor is less than the target conversion of silicon precursor and the pressure in the reactor is increased to increase the calculated conversion of silicon precursor to a target conversion of silicon precursor. After 90 % of the target silicon content is deposited the calculated conversion of silicon precursor is less than the target conversion of silicon precursor and the pressure in the reactor is increased to increase the calculated conversion of silicon precursor to a target conversion of silicon precursor until 100 % of the target silicon content is deposited.

20 In Figures 5 and 6, silicon precursor is injected into the reactor at conditions effective to cause deposition of silicon in the pores of the porous particles and the pressure is increased to increase the calculated conversion of silicon precursor to a target conversion of silicon precursor. After 5 % of the target silicon content is deposited the calculated conversion of silicon precursor remains at the target conversion of silicon precursor. After 60 % of the target silicon content is deposited the calculated conversion of silicon precursor is less than the target conversion of silicon precursor and the pressure in the reactor is increased to increase the calculated conversion of silicon precursor to a target conversion of silicon precursor until 100 % of the target silicon content is deposited.

25 In Figures 7 and 8, silicon precursor is injected into the reactor at conditions effective to cause deposition of silicon in the pores of the porous particles and the pressure is increased to increase the calculated conversion of silicon precursor to a target conversion of silicon precursor. After 5 % of the target silicon content is deposited the calculated conversion of silicon precursor is less than the target conversion of silicon precursor and the pressure in the reactor is increased to increase the calculated conversion of silicon precursor to a target conversion of silicon precursor until 100 % of the target silicon content is deposited.

In Figures 9 and 10, silicon precursor is injected into the reactor at conditions effective to cause deposition of silicon in the pores of the porous particles at a pressure where the calculated conversion of silicon precursor is at a target conversion of silicon precursor. After 70 % of the target silicon content is deposited the calculated conversion of silicon precursor is less than the target conversion of silicon precursor and the pressure in the reactor is increased to increase the calculated conversion of silicon precursor to a target conversion of silicon precursor. After 90 % of the target silicon content is deposited the calculated conversion of silicon precursor is less than the target conversion of silicon precursor and the pressure in the reactor is increased to increase the calculated conversion of silicon precursor to a target conversion of silicon precursor until 100 % of the target silicon content is deposited.

CLAIMS

1. A process for preparing composite particles, the process comprising the steps of:
 - (a) providing a plurality of porous particles in a reactor;
 - 5 (b) contacting the plurality of porous particles with a silicon precursor gas at conditions effective to cause deposition of silicon in the pores of the porous particles;
 - (c) measuring the composition of an effluent gas withdrawn from the reactor;
 - (d) detecting a change in the composition of the effluent gas;
 - (e) adjusting at least one gas outlet of the reactor to adjust the flow rate of the effluent
 - 10 gas to increase the pressure in the reactor in response to the detected change in the composition of the effluent gas and continuing deposition of silicon in the pores of the porous particles at the adjusted pressure;

to provide composite particles comprising a porous particle framework and silicon within the pores of the porous particle framework;
- 15 wherein the silicon precursor gas is introduced into the reactor continuously during steps (b) to (e).
2. A process according to claim 1, wherein the pressure in the reactor is increased in response to detecting an increase in the concentration of the silicon precursor in the effluent gas.
- 20 3. A process according to any preceding claim, wherein the pressure in the reactor is increased in response to detecting a decrease in the concentration of a by-product gas in the effluent gas, optionally wherein the by-product gas is hydrogen.
4. A process according to any preceding claim, wherein the porous particles are mechanically agitated during steps (b) to (e), preferably wherein the porous particles are
- 25 continuously mechanically agitated during steps (b) to (e), more preferably wherein the porous particles are mechanically fluidised during steps (b) to (e).
5. A process according to any preceding claim, wherein step (d) further comprises:

calculating the conversion of the silicon precursor;

comparing the calculated conversion of silicon precursor with a target conversion of silicon precursor; and

determining that the calculated conversion of silicon precursor is less than the target
5 conversion of silicon precursor;

and step (e) further comprises increasing the pressure in the reactor such that the conversion of silicon precursor is increased to at least the target conversion of silicon precursor.

6. A process according to claim 5, wherein the target conversion of silicon precursor is
10 at least 60 %, or at least 70 %, or at least 80 %, or at least 90 %, or at least 95 %, or at least 97 %, or at least 99 %, or 100 %.

7. A process according to claim 5 or 6, wherein the pressure in the reactor is increased by at least $[50 \text{ kPa} \times \Delta X]$, wherein ΔX represents the difference between the calculated conversion of silicon precursor in % and the target conversion of silicon precursor in %, or
15 the pressure in the reactor is increased by at least $[60 \text{ kPa} \times \Delta X]$, or the pressure in the reactor is increased by at least $[70 \text{ kPa} \times \Delta X]$, or the pressure in the reactor is increased by at least $[80 \text{ kPa} \times \Delta X]$, or the pressure in the reactor is increased by at least $[90 \text{ kPa} \times \Delta X]$, or the pressure in the reactor is increased by at least $[100 \text{ kPa} \times \Delta X]$.

8. A process according to any one of claims 5 to 7, wherein the pressure in the reactor is increased by no more than $[3000 \text{ kPa} \times \Delta X]$, wherein ΔX represents the difference between the calculated conversion of silicon precursor in % and the target conversion of silicon precursor in %, or the pressure in the reactor is increased by no more than $[2000 \text{ kPa} \times \Delta X]$, or the pressure in the reactor is increased by no more than $[1000 \text{ kPa} \times \Delta X]$, or the pressure in the reactor is increased by no more than $[500 \text{ kPa} \times \Delta X]$, or the pressure in
20 the reactor is increased by no more than $[400 \text{ kPa} \times \Delta X]$, or the pressure in the reactor is increased by no more than $[300 \text{ kPa} \times \Delta X]$, or the pressure in the reactor is increased by no more than $[200 \text{ kPa} \times \Delta X]$.

9. A process according to any preceding claim, wherein step (d) further comprises:

calculating the partial pressure of silicon precursor in the reactor;

comparing the calculated partial pressure of silicon precursor with a target partial pressure of silicon precursor; and

determining that the calculated partial pressure is less than the target partial pressure of silicon precursor;

5 and step (e) further comprises increasing the pressure in the reactor such that the partial pressure of silicon precursor is increased to at least the target partial pressure of silicon precursor.

10. A process according to claim 9, wherein the target partial pressure of silicon precursor is at least 10 kPa, or at least 20 kPa, or at least 30 kPa, or at least 40 kPa, or at
10 least 50 kPa.

11. A process according to claim 9 or 10, wherein the target partial pressure of silicon precursor is no more than 5000 kPa, or no more than 4000 kPa, or no more than 3000 kPa, or no more than 2000 kPa, or no more than 1600 kPa, or no more than 1500 kPa, or no more than 1200 kPa, or no more than 1000 kPa, or no more than 900 kPa, or no more than
15 800 kPa, or no more than 700 kPa, or no more than 600 kPa, or no more than 500 kPa, or no more than 400 kPa, or no more than 300 kPa, or no more than 250 kPa, or no more than 200 kPa, or no more than 150 kPa.

12. A process according to any preceding claim, wherein the pressure in step (e) is at least 10 % greater than the pressure in step (b), or at least 20 % greater, or at least 30 % greater, or at least 40 % greater, or at least 50 % greater, or at least 60 % greater, or at
20 least 70 % greater, or at least 80 % greater, or at least 90 % greater, or at least 95 % greater.

13. A process according to any preceding claim, wherein the pressure in step (e) is no more than 5000 % greater than the pressure in step (b), or no more than 4000 % greater, or no more than 3000 % greater, or no more than 2000 % greater, or no more than 1000 % greater, or no more than 900 % greater, or no more than 800 % greater, or no more than
25 700 % greater, or no more than 600 % greater, or no more than 500 % greater, or no more than 400 % greater, or no more than 300 % greater, or no more than 175 % greater, or no more than 150 % greater, or no more than 125 % greater, or no more than 100 % greater.

14. A process according to any preceding claim, wherein the pressure in step (b) and/or
30 step (e) is at least atmospheric pressure (about 101 kPa), or at least 105 kPa, or at least 110 kPa, or at least 115 kPa, or at least 120 kPa, or at least 150 kPa, or at least 200 kPa,

or at least 250 kPa, or at least 300 kPa, or at least 400 kPa, or at least 500 kPa, or at least 600 kPa.

15. A process according to any preceding claim, wherein the pressure in step (b) and/or step (e) is no more than 5000 kPa, or no more than 4000 kPa, or no more than 3000 kPa,
5 or no more than 2000 kPa, or no more than 1600 kPa, or no more than 1500 kPa, or no more than 1200 kPa, or no more than 1000 kPa, or no more than 900 kPa, or no more than 800 kPa.

16. A process according to claim 14 or 15, wherein the pressure in step (b) and step (d) is at least 150 kPa and the reactor is a stirred-tank reactor.

10 17. A process according to any preceding claim, wherein the composite particles comprise a target silicon content and 5 to 95 % of the target silicon content is deposited in step (b).

18. A process according to claim 17, wherein the target silicon content is 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
15 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.

19. A process according to claim 17 or 18, wherein the target silicon content is no more than 70 wt% silicon, or no more than 65 wt% silicon, or 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,
20 or no more than 54 wt% silicon.

20. A process according to any one of claims 17 to 19, wherein at least 10 % of the target silicon content is deposited in step (b), or at least 15 %, or at least 20 %, or at least 25 %, or at least 30 %, or at least 35 %, or at least 40 %, or at least 45 %, or at least 50 %, or at least 55 %, or at least 60 %, or at least 65 %, or at least 70 %, or at least 75 %, or at
25 least 80 %, or at least 85 %, or at least 90 %.

21. A process according to any one of claims 17 to 20, wherein no more than 90 % of the target silicon content is deposited step (b), or no more than 85 %, or no more than 80 %, or no more than 75 %, or no more than 70 %, or no more than 65 %, or no more than 60 %, or no more than 55 %, or no more than 50 %, or not more than 45 %, or no more than
30 40 %, or no more than 35 %, or no more than 30 %, or no more than 25 %, or no more than 20 %, or no more than 15 %, or no more than 10 %.

22. A process according to any preceding claim, wherein the ratio of the volume of the porous particles to the volume of the reactor in step (a) is at least 20 cm³ per litre of reactor volume (cm³/L_{RV}), or at least 50 cm³/L_{RV}, or at least 80 cm³/L_{RV}, or at least 100 cm³/L_{RV}, or at least 150 cm³/L_{RV}, or at least 200 cm³/L_{RV}, or at least 250 cm³/L_{RV}, or at least 300 cm³/L_{RV},
5 or at least 400 cm³/L_{RV}, or at least 500 cm³/L_{RV}, or at least 600 cm³/L_{RV}, or at least 700 cm³/L_{RV}, or at least 800 cm³/L_{RV}, or at least 900 cm³/L_{RV}.

23. A process according to any preceding claim, wherein the bed depth of the porous particles in the reactor in step (a) is at least 11 cm, or at least 15 cm, or at least 20 cm, or at least 25 cm, or at least 30 cm.

10 24. A process according to any preceding claim, wherein the ratio of the internal surface area of the reactor to mass of porous particles in the reactor in step (a) is no more than 1 m²/kg, or no more than 0.9 m²/kg, or no more than 0.8 m²/kg, or no more than 0.7 m²/kg, or no more than 0.6 m²/kg, or no more than 0.5 m²/kg, or no more than 0.4 m²/kg, or no more than 0.3 m²/kg.

15 25. A process according to any preceding claim, wherein the flow rate of the silicon precursor gas into the reactor is maintained during steps (b) to (e).

26. A process according to claim 25, wherein the percent deviation in the flow rate of the silicon precursor gas into the reactor is no more than 18 %, or no more than 15 %, or no more than 10 %, or no more than 5 %, or no more than 3 %, or no more than 2 %, or no
20 more than 1 %.

27. A process according to any preceding claim, wherein the flow rate of the silicon precursor gas into the reactor during steps (b) to (e) in grams of silicon in the silicon precursor per minute per kilogram of porous particles is from 0.2 to 25 gmin⁻¹kg⁻¹, or from 0.5 to 20 gmin⁻¹kg⁻¹, or from 1 to 15 gmin⁻¹kg⁻¹, or from 1 to 14 gmin⁻¹kg⁻¹, or from 1 to 13
25 gmin⁻¹kg⁻¹, or from 1 to 12 gmin⁻¹kg⁻¹, or from 2 to 12 gmin⁻¹kg⁻¹, or from 3 to 12 gmin⁻¹kg⁻¹, or from 3 to 11 gmin⁻¹kg⁻¹.

28. A process according to claim 27, wherein the flow rate of the silicon precursor gas into the reactor during steps (b) to (e) in grams of silicon in the silicon precursor per minute per kilogram of porous particles is from 0.2 to 5 gmin⁻¹kg⁻¹, or from 0.2 to 4 gmin⁻¹kg⁻¹, or
30 from 0.2 to 3 gmin⁻¹kg⁻¹.

29. A process according to any preceding claim, wherein the flow rate of the silicon precursor gas into the reactor during steps (b) to (e) in grams of silicon in the silicon precursor per minute per litre of reactor volume ($\text{gmin}^{-1}/\text{L}_{\text{RV}}$) is from 0.03 to $40 \text{ gmin}^{-1}/\text{L}_{\text{RV}}$, or from 0.04 to $35 \text{ gmin}^{-1}/\text{L}_{\text{RV}}$, or from 0.05 to $30 \text{ gmin}^{-1}/\text{L}_{\text{RV}}$, or from 0.06 to $25 \text{ gmin}^{-1}/\text{L}_{\text{RV}}$,
5 or from 0.07 to $20 \text{ gmin}^{-1}/\text{L}_{\text{RV}}$, or from 0.08 to $15 \text{ gmin}^{-1}/\text{L}_{\text{RV}}$, or from 0.09 to $10 \text{ gmin}^{-1}/\text{L}_{\text{RV}}$, or from 0.1 to $5 \text{ gmin}^{-1}/\text{L}_{\text{RV}}$, or from 0.1 to $1 \text{ gmin}^{-1}/\text{L}_{\text{RV}}$, or from 0.15 to $1 \text{ gmin}^{-1}/\text{L}_{\text{RV}}$, or from 0.15 to $0.95 \text{ gmin}^{-1}/\text{L}_{\text{RV}}$, or from 0.2 to $0.95 \text{ gmin}^{-1}/\text{L}_{\text{RV}}$, or from 0.2 to $0.9 \text{ gmin}^{-1}/\text{L}_{\text{RV}}$.
30. A process according to any preceding claim, wherein the range in the temperature during steps (b) to (e) is no more than 50°C , or no more than 40°C , or no more than 30
10 $^{\circ}\text{C}$, or no more than 20°C , or no more than 10°C .
31. A process according to any preceding claim, wherein the temperature during steps (b) to (e) is maintained in the range from 340 to 500°C , or from 350 to 500°C , or from 350 to 480°C , or from 350 to 450°C , or from 350 to 420°C , or from 340 to 400°C , or from 340 to 395°C , or from 340 to 390°C , or from 345 to 400°C , or from 345 to 395°C , or from 345
15 to 390°C , or from 350 to 400°C , or from 350 to 395°C , or from 350 to 390°C , or from 350 to 385°C , or from 350 to 380°C , or from 355 to 400°C , or from 355 to 395°C , or from 355 to 390°C , or from 355 to 385°C , or from 355 to 380°C , or from 360 to 400°C , or from 360 to 395°C , or from 360 to 390°C , or from 360 to 385°C , or from 360 to 380°C , or from 365 to 400°C , or from 365 to 395°C , or from 365 to 390°C , or from 365 to 385°C , or from 365
20 to 380°C , or from 370 to 400°C , or from 370 to 395°C , or from 370 to 390°C , or from 370 to 385°C , or from 375 to 385°C .
32. A process according to any preceding claim, wherein the range in concentration of silicon precursor in the silicon precursor gas introduced into the reactor during steps (b) to (e) is no more than $20 \text{ vol}\%$, or no more than $10 \text{ vol}\%$, or no more than $5 \text{ vol}\%$, or no more
25 than $3 \text{ vol}\%$, or no more than $2 \text{ vol}\%$, or no more than $1 \text{ vol}\%$.
33. A process according to any preceding claim, wherein the silicon precursor gas introduced into the reactor during steps (b) to (e) comprises at least $20 \text{ vol}\%$ silicon precursor, or at least $30 \text{ vol}\%$, or at least $40 \text{ vol}\%$, or at least $50 \text{ vol}\%$, or at least $60 \text{ vol}\%$, or at least $70 \text{ vol}\%$, or at least $80 \text{ vol}\%$, or at least $90 \text{ vol}\%$, or at least $95 \text{ vol}\%$, or at least
30 $98 \text{ vol}\%$, or at least $99 \text{ vol}\%$, or at least $99.9 \text{ vol}\%$, or at least $99.99 \text{ vol}\%$, or $100 \text{ vol}\%$.

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

5 35. A process according to any preceding claim, wherein steps (c) to (e) are repeated one or more times.

36. A process according to any preceding claim, further comprising:

contacting the composite particles with a carbon precursor gas at conditions that are effective to cause deposition of carbon within the pores and/or on the surface of the composite particles.

10 37. A process according to any preceding claim, further comprising:

contacting the composite particles with a passivating agent under conditions that are effective to passivate the composite particles.