

Particulate porous frameworks

Introduction

This invention relates to particulate porous frameworks with optimised pore structures. The frameworks are particularly suited for preparing composite particles for use as anode electroactive materials in metal-ion batteries, such as lithium-ion batteries.

Background

Lithium-ion batteries (LIBs) comprise in general 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. 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 terms "cathode" and "anode" are therefore used herein in the sense that the battery is placed across a load, such that the anode is the negative electrode. The term "battery" is used herein to refer both to devices containing a single cell, e.g. a Li-ion or Na-ion cell, and to devices containing multiple connected cells.

Conventional LIBs use graphite as the anode electroactive material. Graphite anodes can accommodate a maximum of one lithium atom for every six carbon atoms resulting in a maximum theoretical specific capacity of 372 mAh/g in a lithium-ion battery, with a practical capacity that is somewhat lower (ca. 340 to 360 mAh/g). Silicon is a promising alternative to graphite because of its very high capacity for lithium (see, for example, Insertion Electrode Materials for Rechargeable Lithium Batteries, Winter, M. et al. in Adv. Mater. 1998, 10, No. 10). Silicon has a theoretical maximum specific capacity of about 3,600 mAh/g in a lithium-ion battery (based on $\text{Li}_{15}\text{Si}_4$). However, such a high ratio of intercalated lithium to silicon results in expansion of the silicon material by up to 400% of its original volume. Repeated charging and discharging cycles result in significant mechanical stress on the silicon material leading to fracturing and structural failure. Furthermore, the charging of anodes in LIBs results in the formation of a solid electrolyte interphase (SEI) layer. This SEI layer is an ion-conductive yet insulating layer that is formed by the reductive decomposition of electrolytes on exposed electrode surfaces during the initial charge. In a graphite anode, this SEI layer is relatively stable during subsequent charge/discharge cycles. However, the expansion and contraction of a silicon anode results in fracturing and delamination of the SEI layer and the exposure of fresh silicon surface, resulting in further electrolyte decomposition, 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.

One approach to addressing these problems reported by the present inventors is 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 highly porous particles, e.g. a porous carbon material, having a carefully controlled pore size distribution. For example, WO2020/095067, WO2020/128495, and WO2022/029422 report that the improved electrochemical performance of these materials can be attributed to the way in which the electroactive materials form small domains with dimensions of the order of a few nanometres or less within the pore network of the porous particles, which thus function as a framework for the composite particles. Firstly, the fine electroactive structures are thought to have a lower resistance to elastic deformation and higher fracture resistance than larger electroactive structures, and are therefore able to lithiate and delithiated without excessive structural stress. As a result, the electroactive materials exhibit good reversible capacity retention over multiple charge-discharge cycles. Secondly, by controlling the loading of silicon within the porous particle framework such that only part of the pore volume is occupied by silicon in the uncharged state, the unoccupied pore volume of the porous particle framework is able to accommodate a substantial amount of silicon expansion internally. Excessive expansion is constrained by the particle framework. Furthermore, only a small area of the electroactive material surface is accessible to electrolyte and so SEI formation is substantially prevented.

However, a wide variety of feedstocks and synthetic methods exist for obtaining the porous materials used as the frameworks for this type of composite particles. Although desirable pore size distribution parameters for the frameworks have now been reported by the present inventors, it can be difficult to determine which porous materials would be expected to provide a particularly advantageous framework for preparing composite particles, without the laborious process of making many batches of composite particles and performing electrochemical testing on each. Therefore, there remains a need to further optimise the pore structure of the frameworks to further improve the properties of the composite particles prepared therefrom. Moreover, there remains a need to efficiently and reliably assess whether a new source of porous frameworks will be suitable for use in preparing composite particles with desirable properties for downstream uses in LIBs.

Summary of the invention

The invention provides a process comprising the steps of:

(a) determining an effective size σ of a silicon precursor;

(b) providing a population of optimised particulate porous frameworks comprising micropores and/or mesopores and having an optimised pore structure for the silicon precursor, the optimised pore structure comprising:

a PD₃₀ pore diameter of 1.4σ - 3.0σ ,

5 a PD₉₀ pore diameter of 5.0σ - 14.0σ , and

a pore diameter span (PD₉₀-PD₁₀) of 4.0σ - 12.0σ ,

wherein "effective size σ " refers to the value σ in the Lennard-Jones potential for the silicon precursor;

10 wherein "PD_n pore diameter" refers to the pore diameter below which n% of the total micropore and mesopore volume is found.

The inventors have found that the pore structure of a framework is optimised for use with a silicon precursor when the pore diameter distribution is controlled to be within certain limits, based on multiples of the effective size of the silicon precursor. In this way, the frameworks are optimised for

15 a subsequent silicon deposition step utilising the silicon precursor, providing composite particles for use as an electroactive material for a metal-ion battery. The optimised pore structure facilitates the formation of composite particles with desirable properties for this use, e.g. with a high percentage of surface silicon, as shown by the present examples. Moreover, the understanding provided by the inventors of how to select porous frameworks having an optimised pore structure may

20 advantageously be used to screen multiple sources of frameworks, and multiple silicon precursors, and select those which will be expected to provide composite particles with desirable properties.

The invention provides optimised particulate porous frameworks comprising micropores and/or mesopores and having the optimised pore structure for a silicon precursor.

25 Composite particles are also provided, such as those obtainable from the optimised particulate porous frameworks and the silicon precursor. Thus, the invention preferably further comprises the step of: (c) contacting the optimised particulate porous frameworks provided by step (b) with the silicon precursor of step (a) at a temperature effective to cause deposition of elemental silicon in

30 the pores of the optimised particulate porous frameworks, thereby providing composite particles. The invention also provides electrodes comprising the composite particles, rechargeable metal-ion batteries comprising the electrodes, and processes for making the same.

Figures

35 Figure 1 shows the TGA trace for the composite particles prepared from carbon frameworks C15 and C16 in Example 1.

Figure 2 shows the average surface silicon and PD₃₀ values for the composite particles prepared in Example 1.

Figure 3 shows the average surface silicon and PD₉₀ values for the composite particles prepared in Example 1.

5 Figure 4 shows the average surface silicon and (PD₉₀ - PD₁₀) values for the composite particles prepared in Example 1.

Figure 5 shows the surface silicon and PD₃₀ values for the composite particles prepared in Example 2.

10 Figure 6 shows the surface silicon and PD₉₀ values for the composite particles prepared in Example 2.

Figure 7 shows the surface silicon and (PD₉₀ - PD₁₀) values for the composite particles prepared in Example 2.

Figure 8 shows the surface silicon and PD₃₀ values for the composite particles prepared in Example 3.

15 Figure 9 shows the surface silicon and PD₉₀ values for the composite particles prepared in Example 3.

Figure 10 shows the surface silicon and (PD₉₀ - PD₁₀) values for the composite particles prepared in Example 3.

20 Detailed description of the invention

It will be understood that the steps of the processes herein are labelled for ease of reference.

Unless clearly incompatible the steps may be performed in any order, with or without other intervening steps. The description below of the particulate porous frameworks, silicon precursors, composite particles, electrodes, batteries etc. applies equally to these items provided as products
25 per se or when used as part of a process.

The optimised pore structure has been determined by the inventors on the basis that depositing silicon in porous frameworks may be efficiently performed by a chemical vapour infiltration process (CVI). This is a variant of chemical vapour deposition (CVD) where the decomposition surface is
30 within a pore inside a porous framework. For decomposition of a silicon precursor into silicon to occur, the precursor must be able to enter the pore of the framework and travel to a suitable decomposition site. Desirable frameworks generally 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
35 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.

The inventors have determined that the pores sizes that are most suitable for porous frameworks to form high-performing composite particles after CVI can be obtained by controlling the size of the pores based on the size of the silicon precursor. This is due to the realisation that the transport of a silicon precursor within a porous framework is influenced by the diameter of the pores and the size of the precursor. As pores become ever smaller the interaction between the silicon precursor and the pore walls begins to control the behaviour. For CVI to be successful in microporous and mesoporous systems, the silicon precursor must be able to enter the pore in order to adsorb, i.e. the pore should be bigger than the molecule of interest. In order to be able to deposit meaningful amounts of silicon the precursor molecules need to be able to move in the pore, i.e. there must be extra space so that transport of the precursor throughout the pore system can occur without being blocked by precursor molecules which have already adsorbed. There must also be a minimum amount of space left after a precursor molecule has decomposed to allow further precursor transport and decomposition to form silicon. Essentially, pores must be wide enough to allow precursor transport throughout the framework and there must sufficient pore volume to accommodate the desired quantity of silicon for the application. However, once transport into the pore is considered, a further factor is that precursor molecules impact each other and also the walls of the pore system. Where the pores are sufficiently narrow, it is believed that interaction between precursor molecules and the pore wall becomes dominant in determining the transport properties, such that the adsorbed molecules is held in the pore by dispersion forces with the walls. These interaction forces are believed to become the dominant consideration where the molecular dimensions are on the same order of magnitude as the width of the pore. Thus, the span of the pore sizes is also important such that there are not too many pores at small or large sizes, relative to the size of the precursor. In view of these realisations, the inventors have determined that a pore structure is optimised for CVI based on a pore diameter distribution defined by certain multiples of the size of the precursor.

The silicon precursor is most preferably a gaseous silicon precursor as these may be conveniently used in CVI processes. The gaseous silicon precursor may be selected from silane (SiH_4), disilane (Si_2H_6), trisilane (Si_3H_8), tetrasilane (Si_4H_{10}), pentasilane (Si_5H_{12}), hexasilane (Si_6H_{14}), methylsilane (CH_3SiH_3), dimethylsilane ($(\text{CH}_3)_2\text{SiH}_2$), trimethylsilane ($(\text{CH}_3)_3\text{SiH}$), tetramethylsilane ($(\text{CH}_3)_4\text{Si}$), or chlorosilanes such as trichlorosilane (HSiCl_3) or dichlorosilane (H_2SiCl_2) or chlorosilane (H_3SiCl), or methylchlorosilanes such as methyltrichlorosilane (CH_3SiCl_3) or dimethyldichlorosilane ($(\text{CH}_3)_2\text{SiCl}_2$). Preferably the silicon precursor is selected from silane (SiH_4), disilane (Si_2H_6),

trisilane (Si_3H_8), tetrasilane (Si_4H_{10}). A particularly preferred silicon precursor is silane (SiH_4). However, in one implementation the silicon precursor is not silane (SiH_4), and optionally is not silane (SiH_4) or disilane (Si_2H_6).

- 5 The effective size σ of the silicon precursor is the value σ in the Lennard-Jones potential for the silicon precursor. σ is typically expressed in nm. The Lennard-Jones potential is a widely known intermolecular pair potential for identical particles, typically in a gaseous state, defined as:

$$V_{LJ}(r) = 4\varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]$$

- 10 where r is the distance between two identical interacting particles, ε is the depth of the potential well, and σ is the distance at which the particle-particle potential energy V is zero. ε is sometimes known as the dispersion energy. σ is sometimes known as the collision or Van der Waals diameter.

- The effective size is believed to be invariant to the conditions, e.g. invariant to temperature and pressure. Nevertheless, if needed the effective size can be specified as at room temperature
15 (25 °C) and atmospheric pressure (101,325 Pa).

- Preferably, σ is a value in the range of 0.4-0.6 nm. Values of σ for many silicon precursors are reported in the literature (Gorbachev *et al.*, *Technical Physics* 2000, 45(8), 1032-1041; Noda *et al.*, *Int J Chem Kinet.* 2021, 53, 1036–1049; J. Perrin *et al.*, *Contrib. Plasma Phys.* 1996, 36 (3), 3).
20 Values for σ may also be calculated from thermodynamic data available in the literature e.g. in Kee *et al.*, *CHEMKIN Collection*, Release 3.6, Reaction Design, Inc., San Diego, CA (2000). The effective size for some silicon precursors is listed in the table below. Any of these precursors may be used in the invention.

Silicon precursor	Effective size σ (nm)
SiH_4	0.408
Si_2H_6	0.483
Si_3H_8	0.556
HSiCl_3	0.564
H_2SiCl_2	0.503
H_3SiCl	0.415

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The optimised pore structure comprises:

- a PD_{30} pore diameter of 1.4σ - 3.0σ , or preferably 1.6σ - 3.0σ , or 1.7σ - 2.8σ , or 1.8σ - 2.2σ ;
a PD_{90} pore diameter of 5.0σ - 14.0σ , or 6.0σ - 13.5σ , or 8.5σ - 13.0σ ; and

a pore diameter span (PD_{90} - PD_{10}) of 4.0σ - 12.0σ , or 4.5σ - 11.5σ , or 6.0σ - 11.0σ .

The optimised pore structure is thus defined relative to the effective size of the silicon precursor. In this way, each silicon precursor having a different effective size gives a different optimised pore structure.

In a particular example, the optimised pore structure comprises:

a PD_{30} pore diameter of 1.6σ - 3.0σ ;

a PD_{90} pore diameter of 5.0σ - 14.0σ ;

a pore diameter span (PD_{90} - PD_{10}) of 4.0σ - 12.0σ ; and

a total volume of micropores and mesopores in the range from 0.4 to 1.8 cm³/g.

In another particular example, the optimised pore structure comprises:

a PD_{30} pore diameter of 1.7σ - 2.8σ ;

a PD_{90} pore diameter of 6.0σ - 13.5σ ; and

a pore diameter span (PD_{90} - PD_{10}) of 4.5σ - 11.5σ .

In another particular example, the optimised pore structure comprises:

a PD_{30} pore diameter of 1.6σ - 3.0σ ;

a PD_{90} pore diameter of 5.0σ - 14.0σ ;

a pore diameter span (PD_{90} - PD_{10}) of 4.0σ - 12.0σ ; and

a total volume of micropores and mesopores in the range from 0.4 to 1.8 cm³/g;

the particulate porous frameworks are particulate porous carbon frameworks having a D_{50} particle diameter of less than 30 μ m; and

silicon precursor in step (a) is silane (SiH_4) and the effective size σ is 0.408 nm.

The optimised pore structure may further comprise one or both of:

a PD_{50} pore diameter of $<4.0\sigma$ or $<3.7\sigma$, and

a PD_{75} pore diameter of 3.75σ - 8.0σ or 5.0σ - 7.0σ .

The optimised pore structure may include a monomodal, bimodal or multimodal pore size distribution. 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 particulate porous frameworks. A bimodal or multimodal pore size distribution is preferred since close proximity between micropores and pores of larger diameter provides the advantage of efficient ionic transport through the porous network to the electroactive material.

Preferably, the bimodal or multimodal pore size distribution has peaks in at least two of, optionally in all three of, regions (i) 1.2σ - 1.7σ (ii) 1.8σ - 2.1σ , and (iii) 2.2σ - 3.2σ . These peaks typically include at least the two most intense peaks, optionally the three most intense peaks, in the pore size distribution. The intensity ratio of peak (i) : peak (iii) is preferably $> 0.5:1$. The intensity ratio of peak (i) : peak (ii) is preferably $< 5:1$.

The general term “PD_n pore diameter” refers herein to the volume-based nth percentile pore diameter, based on the total volume of micropores and mesopores. For instance, the term “PD₅₀ pore diameter” as used herein refers to the pore diameter below which 50% of the total micropore and mesopore volume is found. For the avoidance of doubt, any macropore volume (pore diameter greater than 50 nm) is not taken into account for the purpose of determining PD_n values.

The total volume of micropores and mesopores and the pore size distribution of micropores and mesopores, including the P¹ and PD_n pore diameter parameters defined herein, are determined using nitrogen gas adsorption at 77 K down to a relative pressure p/p_0 of 10^{-6} using quenched solid density functional theory (QSDFT), preferably in accordance with standard methodology as set out in ISO 15901-2 and ISO 15901-3, most preferably ISO 15901-2:2022. Nitrogen gas adsorption is a technique that characterises the porosity and pore diameter distributions of a material by allowing a gas to condense in the pores of a solid. As pressure increases, the gas condenses first in the pores of smallest diameter and the pressure is increased until a saturation point is reached at which all of the pores are filled with liquid. The nitrogen gas pressure is then reduced incrementally, to allow the liquid to evaporate from the system. Analysis of the adsorption and desorption isotherms, and the hysteresis between them, allows the pore volume and pore size distribution to be determined. Suitable instruments for the measurement of pore volume and pore size distributions by nitrogen gas adsorption include the TriStar II and TriStar II Plus porosity analyzers, which are available from Micromeritics Instrument Corporation, USA, and the Autosorb IQ porosity analyzers, which are available from Quantachrome Instruments.

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_n values are likewise 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 particulate porous frameworks 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 0.2 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 electroactive material in micropores and smaller mesopores.

Any pore volume measured by mercury porosimetry at pore sizes of 50 nm or below is disregarded (as set out above, nitrogen adsorption is used to characterize the mesopores and micropores). Pore volume measured by mercury porosimetry above 100 nm is 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 particulate porous frameworks. 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 particulate porous frameworks. 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 optimised particulate porous frameworks may be characterised by the total volume of micropores and mesopores (i.e. the total pore volume in the pore diameter range from 0 to 50 nm). Typically, the optimised particulate porous frameworks include both micropores and mesopores.

5 However, it is not excluded that particulate porous frameworks may be used which include micropores and no mesopores, or mesopores and no micropores.

The optimised pore structure is defined relative to the effective size of a silicon precursor.

10 However, the optimised pore structure may be further defined by absolute values believed to provide for particulate porous frameworks advantageous for use with a variety of silicon precursors, and advantageous for the end-use in LIBs. The optimised pore structure preferably comprises a total volume of micropores and mesopores of at least 0.4 cm³/g, or at least 0.5 cm³/g, or at least 0.6 cm³/g, or at least 0.65 cm³/g, or at least 0.7 cm³/g, or at least 0.75 cm³/g, or at least 0.8 cm³/g. The use of higher porosity particles may be advantageous since it allows a larger
15 amount of electroactive material to be accommodated within the pore volume.

The internal pore volume of the optimised particulate porous frameworks is suitably capped at a value at which increasing fragility of the framework's structure outweighs the advantage of increased pore volume accommodating a larger amount of electroactive material. The optimised
20 pore structure may comprise a volume of micropores and mesopores of no more than 1.8 cm³/g, or no more than 1.7 cm³/g, or no more than 1.6 cm³/g, or no more than 1.55 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.

25 Preferably the optimised pore structure comprises a total volume of micropores and mesopores in the range from 0.4 to 1.8 cm³/g, or from 0.4 to 1.7 cm³/g, or from 0.5 to 1.6 cm³/g, or from 0.5 to 1.55 cm³/g, or from 0.6 to 1.5 cm³/g, or from 0.6 to 1.45 cm³/g, or from 0.65 to 1.4 cm³/g, or from 0.65 to 1.35 cm³/g, or from 0.7 to 1.3 cm³/g, or from 0.7 to 1.25 cm³/g, or from 0.75 to 1.2 cm³/g, or
30 from 0.75 to 1.1 cm³/g, or from 0.8 to 1.2 cm³/g, or from 0.8 to 1.1 cm³/g.

The optimised pore structure may comprise a micropore volume of preferably at least 0.3 cm³/g, or at least 0.4 cm³/g, or at least 0.5 cm³/g, or at least 0.6 cm³/g.

35 The micropore volume fraction of the optimised pore structure may be at least 0.4, or at least 0.45, or at least 0.5, or at least 0.55, or at least 0.6, and/or no more than 0.95, or no more than 0.9, or no

more than 0.85, or no more than 0.8, based on the total volume of micropores and mesopores in the optimised particulate porous frameworks.

The optimised pore structure may have a modal pore diameter of micropores and mesopores of ≥ 0.50 nm preferably ≥ 0.60 nm.

The total volume of micropores and mesopores (i.e. the total pore volume of pores having a diameter in the range of 0 to 50 nm) may be referred to as P^1 cm³/g. In the case that the particulate porous frameworks comprise macropores, the volume of pores in the range of greater than 50 nm and up to 100 nm may be referred to as P^2 cm³/g and is measured by mercury porosimetry. The volume of macropores (and therefore the value of P^2) is preferably small as compared to the volume of micropores and mesopores (and therefore the value of P^1). While a small fraction of macropores may be useful to facilitate electrolyte access into the pore network, the advantages of the invention are obtained substantially by accommodating silicon in micropores and smaller mesopores. Thus, in the optimised pore structure, P^2 preferably has a value of up to $0.2 \times P^1$, or up to $0.1 \times P^1$, or up to $0.05 \times P^1$, or up to $0.02 \times P^1$, or up to $0.01 \times P^1$, or up to $0.005 \times P^1$.

One of the advantages of the invention is that the determination of the optimised pore structure provides a convenient and effective way to assess whether new sources of particulate porous frameworks will be expected to provide a starting material for preparing composite particles having excellent properties for use in metal-ion batteries. This may be achieved by measuring the pore structure of the frameworks, e.g. by the routine means described herein, to determine whether the optimised pore structure is present, without the need for the expensive and time-consuming steps of depositing silicon in the frameworks and conducting electrochemical testing to assess the performance of the resulting composite particles. If the optimised pore structure is present the frameworks are then accepted for subsequent use. If the optimised pore structure is not present the frameworks are then rejected. The pore structure of a different source of frameworks may then be measured. Once a population of optimised particulate porous frameworks has been identified, silicon can be deposited within the pores using the silicon precursor of step (a), thereby providing composite particles.

Thus, step (b) may include the steps of:

(b1) providing one or more populations of particulate porous frameworks comprising micropores and/or mesopores;

(b2) measuring the pore structure of each population;

(b3) accepting each population that has the optimised pore structure and rejecting each population that does not have the optimised pore structure; and

(b4) using one or more of the accepted populations as the population of optimised particulate porous frameworks or, if no populations are accepted, repeating steps (b1), (b2), and (b3) on a further population of particulate porous frameworks comprising micropores and/or mesopores until a population is accepted.

The silicon precursor and the population of optimised particulate porous frameworks may then be provided as a kit. The components of the kit may be held separately until, preferably, the silicon precursor is used to deposit silicon in the pores of the optimised particulate porous frameworks.

A particular advantage of the invention lies in the ability to screen multiple populations of particulate porous frameworks. Thus, preferably, at least two populations are provided in step (b1), optionally at least one of which is rejected in step (b3). The act of rejecting a population of particulate porous frameworks provides a useful technical teaching in that the population does not need to be subjected to further testing.

Optionally, if no populations are accepted after measuring the pore structure of 10 populations, the process may be halted. In this way, useful information has still been provided that the 10 rejected populations do not have the optimised pore structure for the silicon precursor.

Another advantage of the invention is that it allows the silicon precursor to be optimised to available particulate porous frameworks, without the need for the expensive and time-consuming steps of depositing silicon in the frameworks from multiple different precursors and conducting electrochemical testing to assess the performance of the resulting composite particles. In this way, when one particular source of particulate porous frameworks is found to be desirable for other reasons, e.g. if it is low-cost and/or available at large scale, it may be used with an optimised silicon precursor to provide composite particles having excellent properties for use in metal-ion batteries.

Thus, the process of the invention may include:

(a1) providing one or more silicon precursors;

(a2) determining an effective size σ of each silicon precursor;

(b5) providing a population of particulate porous frameworks comprising micropores and/or mesopores;

(b6) measuring the pore structure of the population;

(a3) accepting each silicon precursor that has an effective size such that the pore structure is the optimised pore structure for the silicon precursor and rejecting each silicon precursor that has an effective size is such that the pore structure is not the optimised pore structure for the silicon precursor;

5 (a4) if no silicon precursors are accepted, repeating steps (a1), (a2), and (a3) on a further silicon precursor until a silicon precursor is accepted.

10 It will be understood that once a silicon precursor is accepted in step (a3), the population of particulate porous frameworks provided in step (b5) is the optimised particulate porous frameworks provided in step (b). The accepted silicon precursor and the optimised particulate porous frameworks may then be provided as a kit. The components of the kit may be held separately until, preferably, the accepted silicon precursor is used to deposit silicon in the pores of the particulate porous frameworks.

15 A particular advantage of the invention lies in the ability to screen multiple silicon precursors. Thus, preferably, at least two silicon precursors are provided in step (a1), optionally at least one of which is rejected in step (a3). The act of rejecting a silicon precursor provides a useful technical teaching in that the precursor does not need to be used in further testing on the population of particulate porous frameworks.

20 Optionally, if no silicon precursors are accepted after determining the effective size σ of 10 silicon precursors, the process may be halted. In this way, useful information has still been provided that the particulate porous frameworks do not have the optimised pore structure for the 10 rejected silicon precursors.

25 One of the advantages of the invention is that it allows for the identity of optimised particulate porous frameworks to be determined at a laboratory scale, without the need to provide all feasible particulate porous frameworks at industrial scale before it is known whether they will be suitable for an end use. For example, the populations of optimised particulate porous frameworks provided in steps (b), (b1), and (b5) can be less than 50 kg or less than 10 kg. Once optimised particulate porous frameworks have been identified in the lab they can then be obtained at larger scales with the confidence that they will be suitable for manufacturing large volumes of composite particles having good properties. The process of the invention thus preferably further comprises providing a further population of the optimised particulate porous frameworks at industrial scale. Industrial scale may be defined as at least 100 kg or preferably at least 1,000 kg of the optimised particulate

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porous frameworks. A kit may be provided comprising the further population and the silicon precursor.

In general, the particulate porous frameworks have a D_{50} particle diameter of less than 100 μm , or of less than 30 μm , preferably in the range from 1 to 30 μm . Optionally, the D_{50} particle diameter of the particulate porous frameworks 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 particulate porous frameworks may be 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 .

The D_{10} particle diameter of the particulate porous frameworks is preferably 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 0.5 μm or more, the potential for undesirable agglomeration of sub- micron sized particles is reduced, and improved dispersibility of the composite particles formed.

The D_{90} particle diameter of the particulate porous frameworks is preferably no more than 50 μm , or no more than 40 μm , or no more than 30 μm , or no more than 25 μm , or no more than 20 μm , or no more than 15 μm .

The particulate porous frameworks 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 into dense powder beds is more readily achievable.

The term "particle diameter" as used herein refers to the equivalent spherical diameter (esd), i.e. the diameter of a sphere having the same volume as a given particle, wherein the particle volume is understood to include the volume of any intra-particle pores. The terms " D_{50} " and " D_{50} particle diameter" as used herein refer to the volume-based median particle diameter, i.e. the diameter below which 50% by volume of the particle population is found. The terms " D_{10} " and " D_{10} particle diameter" as used herein refer to the 10th percentile volume-based median particle diameter, i.e. the diameter below which 10% by volume of the particle population is found. The terms " D_{90} " and " D_{90} particle diameter" as used herein refer to the 90th percentile volume-based median particle diameter, i.e. the diameter below which 90% by volume of the particle population is found.

Particle diameters and particle size distributions can be determined by standard laser diffraction techniques in accordance with ISO 13320:2009. Laser diffraction relies on the principle that a particle will scatter light at an angle that varies depending on the size the particle and a collection of particles will produce a pattern of scattered light defined by intensity and angle that can be correlated to a particle size distribution. A number of laser diffraction instruments are commercially available for the rapid and reliable determination of particle size distributions. Unless stated otherwise, particle size distribution measurements as specified or reported herein are as measured by the conventional Malvern Mastersizer™ 3000 particle size analyzer from Malvern Instruments™. The Malvern Mastersizer™ 3000 particle size analyzer operates by projecting a helium-neon gas laser beam through a transparent cell containing the particles of interest suspended in an aqueous solution. Light rays which strike the particles are scattered through angles which are inversely proportional to the particle size and a photodetector array measures the intensity of light at several predetermined angles and the measured intensities at different angles are processed by a computer using standard theoretical principles to determine the particle size distribution. Laser diffraction values as reported herein are obtained using a wet dispersion of the particles in 2-propanol with a 5 vol% addition of the surfactant SPAN™-40 (sorbitan monopalmitate). The particle refractive index is taken to be 2.68 for particulate porous frameworks 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.

The particulate porous frameworks 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. Preferably, the particulate porous frameworks have an average sphericity of at least 0.90, or at least 0.92, or at least 0.93, or at least 0.94, or at least 0.95. Spherical particles are believed to aid uniformity of deposition and facilitate denser packing both in the batch pressure reactor 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:

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

5 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.

10 The particulate porous frameworks preferably have a BET surface area of at least 100 m²/g, or at least 500 m²/g, or at least 750 m²/g, or most preferably 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 methods, e.g. ISO 9277:2022. Preferably, the BET surface area of the particulate porous
15 frameworks 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 particulate porous frameworks may have a BET surface area in the range from 100 m²/g to 4,000 m²/g, or from 500 m²/g to 4,000 m²/g, or from 750 m²/g to 3,500 m²/g, or from 1,000 m²/g to 3,250 m²/g, or from 1,000 m²/g to 3,000 m²/g, or from 1,000 m²/g to 2,500 m²/g, or from 1,000 m²/g
20 to 2,000 m²/g.

The particulate porous frameworks 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
25 “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). Preferably, the particulate porous frameworks 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
30 g/cm³, or at least 0.65 g/cm³, or at least 0.7 g/cm³. Preferably, the particulate porous frameworks 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, or no more than 1 g/cm³, or no more than 0.95 g/cm³, or no more than 0.9 g/cm³.

The particulate porous frameworks preferably comprise a conductive material. The use of conductive particulate porous frameworks is advantageous as they form a conductive framework within the composite particles which facilitates the flow of electrons between lithium atoms/ions inserted into the electroactive material and a current collector.

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A preferred type of particulate porous frameworks comprise or consist of a conductive carbon material, referred to herein as conductive particulate porous carbon frameworks.

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The particulate porous frameworks preferably comprise at least 80 wt% carbon, more preferably at least 85 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.

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As used herein, the term “hard carbon” refers to a disordered carbon matrix in which carbon atoms are found predominantly in the sp^2 hybridised state (trigonal bonds) in nanoscale polyaromatic domains. The polyaromatic domains are cross-linked with a chemical bond, e.g. a C-O-C bond. Due to the chemical cross-linking between the polyaromatic domains, hard carbons cannot be converted to graphite at high temperatures. Hard carbons have graphite-like character as evidenced by the large G-band ($\sim 1600\text{ cm}^{-1}$) in the Raman spectrum. However, the carbon is not fully graphitic as evidenced by the significant D-band ($\sim 1350\text{ cm}^{-1}$) in the Raman spectrum.

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

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When the particulate porous frameworks are particulate porous carbon frameworks, the optimised particulate porous carbon frameworks may have a ratio of the relative intensity of D and G peaks (I_D/I_G) of ≤ 2.0 or ≤ 1.8 as measured by Raman spectroscopy. Alternatively, or in addition, I_D/I_G of the optimised particulate porous carbon frameworks may be ≥ 1 or ≥ 1.05 . For example, I_D/I_G of the optimised particulate porous carbon frameworks may be in the range of 1.0-1.6.

Providing the particulate porous frameworks includes synthesising the frameworks and obtaining the frameworks from a supplier.

Most preferably, the particulate porous frameworks are particulate porous carbon frameworks. The particulate porous carbon frameworks used in the invention are most preferably a form of activated carbon. The term "activated carbon" refers to a carbonaceous material that has been physically or chemically processed to increase its porosity and surface area. Chemical activation or physical activation (e.g. high temperature steam or CO₂) mechanisms are among common methods used in the production of activated carbons. A suitable activation process comprises contacting pyrolyzed carbon with one or more of oxygen, steam, CO, and CO₂ at a temperature in the range from 300 to 1500°C, 600 to 1200°C, or 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.

A variety of different particulate porous carbon frameworks are available in the art depending on the starting material and the conditions of the pyrolysis process. Particulate porous carbon frameworks of various different specifications are available from commercial suppliers.

A variety of different carbonaceous materials may be used to prepare suitable particulate porous carbon frameworks via pyrolysis. Preferably, a plant source is used. Examples of plant sources include the husks and shells of seeds, nuts and fruits (also including drupes, kernels and pits). Examples of these plant sources include the shells and husks of coconuts (including coir), groundnuts, walnuts, apricots, almonds, palm seeds, peaches, olives, hazelnuts, bamboos, and tree barks (e.g. the bark of softwood trees including pine, spruce, larch and poplar, and hardwood trees including oak). A preferred plant source is coconut shells. Fossil carbon sources such as coal may be used. Examples of resins and polymeric materials as carbonaceous materials 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.

The carbonaceous material, e.g. the plant source, preferably has an elemental composition including at least 40 wt% carbon, at least 3 wt% hydrogen and at least 30 wt% oxygen. Trace amounts of nitrogen, sulphur and chlorine may also be present. More preferably, the carbonaceous material has an elemental composition including around 50 wt% carbon, 5 wt% hydrogen and 40 wt% oxygen with lesser amounts of nitrogen, sulphur and chlorine being present.

The particulate porous carbon frameworks are typically obtained from the carbonaceous material in a process comprising two steps. Firstly, the carbonaceous material is pyrolyzed by heating in an inert atmosphere. An inert atmosphere may be an atmosphere of nitrogen, CO₂, a noble gas, and mixtures thereof. Pyrolysis is usually carried out at a temperature of about 400 to 900 °C, or about 500 to 700 °C, or about 550 to 700 °C so that dehydration and devolatilization of the carbon occur. Preferably, the temperature does not exceed about 700 °C. Optionally, the carbonaceous material is pre-treated to remove impurities prior to heating. Optionally, the carbonaceous material is purified and/or washed and dried prior to heating. Optionally, the carbonaceous material is sieved and crushed or milled to obtain uniform sized particles prior to heating. Optionally the carbonaceous material is pelletized before heating.

Secondly, the pyrolyzed material is activated by heating in a flow of one or more of oxygen, steam, CO, and CO₂ at a temperature between 600 °C and 1200 °C. This allows a chemical reaction between the carbon and the flowing gas to take place at the internal surface of the carbon, removing carbon from the pore walls and thereby increasing the pore volume. This gaseous activation process, also known as a physical activation process, allows the pore size to be readily altered producing activated carbons with the desired porosity. Preferably, the pyrolyzed material is activated with steam.

The physical activation may suitably be performed in a rotary furnace, a fixed bed reactor or a fluidized bed reactor. Optionally, additional washing, cleaning or purifying steps may be performed after the activation. Optionally the pyrolyzation and activation steps may be combined into a continuous process. Optionally, the activated material is comminuted (e.g. milled) and/or sieved after the activation step to obtain particles of the desired size.

The burn-off of the pyrolyzed material during activation is preferably at least 30%, or at least 40%. The burn-off is preferably no more than 80%, or no more than 75%, or no more than 70%. The burn-off is the mass fraction of the pyrolyzed material that is removed during the physical activation step, as a percentage of the material mass before physical activation is commenced.

In chemical activation methods the carbonaceous material is impregnated with a chemical activation agent (such as NaOH, KOH, K₂CO₃, H₃PO₄, CaCl₂, ZnCl₂, and mixtures thereof, etc.). The carbonaceous material is typically impregnated prior to pyrolysis and the pyrolysis step takes place simultaneously with the activation, though the carbonaceous material may be carbonized prior to chemical impregnation. Pyrolysis for chemical activation may take place at 250-1000 °C or 500-950 °C. If the porous carbon is formed using chemical activation processes, then, instead of

pores being created by removal of carbon, the activation mechanism works by expanding existing pores or pushing apart graphene sheets (exfoliation) which is not conducive to maintaining a high proportion of micro-pore spaces accessible via narrow channels/openings. This is thought to cause relatively poorer electrochemical performance of composite materials prepared from chemically activated porous carbon materials. Thus, preferably the particulate porous carbon frameworks are prepared by physical activation.

An example of a typical activated carbon synthesis is as below:

Synthetic activated carbons are prepared from a mixture of Novolak resin and 11% of hexamethylenetetramine powder, Bakelite PF 6705 FP, purchased from Hexion GmbH. This starting material is cross-linked at 150 °C for 1 h and the solid blocks of cross-linked material are hammered to 2-3 cm pieces before grinding them to ~100 µm particles. This cured resin powder is then pyrolyzed at 800 °C for 10 min under a nitrogen flow of 1 L/min. The carbon yield obtained from this precursor is 57-59%. After carbonization, the carbon is ball milled to particle size of 3-4 µm and the carbon material obtained has a total pore volume of 0.25–0.3 cm³/g, including 0.20–0.22 cm³/g of microporosity and a surface area of 650–700 m²/g. This carbon is then activated in either steam or CO₂ to achieve a desirable pore volume. Typical activation temperature used for CO₂ activation to achieve 0.8-0.9 cm³/g total pore volume, is 950-980 °C with dwell time of 5-8h depending on the amount of carbon being activated, CO₂ flow rate, and the type of furnace being used. The temperature used for steam activation is lower than CO₂, typically 850 °C, as steam is more reactive. The dwell time at the activation temperature for steam is typically 6-9h depending on the type and amount of charcoal being activated, steam flow rate, and the type of furnace being used.

An example of activated carbon made using steam activation is as follows:

To make steam activated synthetic scaffold with a total pore volume of 0.79 cm³/g, steam is introduced via a humidifier consisting of nitrogen atomizer (3 bar injection pressure) through 1 mm orifice positioned at right angles to a 1 mm orifice which adds water dropwise to an atomization chamber where the high pressure nitrogen stream induces atomization via impingement of the high pressure gas on the water droplet. Heated tapes are used on the inlet and outlet to prevent adventitious steam condensation. Carbonised phenolic resin is ball-milled in a planetary ball mill to D₅₀ = 3 µm (60 g loading, 105, 10 mm balls, 300 RPM, 20 min interval). Subsequently, 15 g of milled carbonised phenolic resin is loaded into a short alumina crucible, the material is spread evenly along the crucible. Steam activation takes place in a tube furnace with the crucible placed in

the middle of the heating zone. The furnace is purged with N₂ at 0.8 L/min for 10-30 minutes. A ramp rate of 8.7 °C/min with a set-point of 850 °C is used. Once the temperature has reached 840 °C, water is injected into an atomisation nozzle at a rate of 0.25 mL/min (water injection volume), temperature is held stable once 850 °C is reached. Dwell for 345 min. When dwell has completed, steam flow is set to zero and heating tape is turned off.

Alternatives to particulate porous carbon frameworks include particulate porous frameworks comprising titanium nitride, titanium carbide, silicon carbide, boron carbide, nickel oxide, silicon oxide, silicon dioxide, aluminium oxide, silicon-aluminium ternary oxides, magnesium oxide, lead oxide, zirconium oxide, silicon nitride, titanium silicon nitride, nickel nitride, molybdenum nitride, titanium oxynitride, silicon oxycarbide, boron nitride, or vanadium nitride. Preferred alternatives to particulate porous carbon frameworks are particulate porous frameworks of titanium nitride, silicon oxycarbide or boron nitride.

The process of the invention preferably further comprises the step of: (c) contacting the optimised particulate porous frameworks provided by step (b) with the silicon precursor of step (a) at a temperature effective to cause deposition of elemental silicon in the pores of the optimised particulate porous frameworks, thereby providing composite particles. In this way, composite particles for use as an electroactive material for a metal-ion battery are prepared.

The particulate porous frameworks provide a framework for the silicon, which is typically deposited in the form of a plurality of electroactive domains. The term "electroactive domain" refers to a body of electroactive material, e.g. elemental silicon, having maximum dimensions that are determined by the dimensions of the micropores and/or mesopores of the particulate porous frameworks in which they are located. The electroactive domains may therefore be described as nanoscale electroactive domains, wherein the term "nanoscale" is understood to refer generally to dimensions less than 100 nm although, due to the dimensions of micropores and mesopores, the electroactive domains typically have maximum dimensions in any direction of less than 50 nm, and usually significantly less than 50 nm. A domain may for example take the form of a regular or irregular particle or a bounded layer or region of coating.

Step (c) is suitably performed via chemical vapor infiltration (CVI) of a gaseous silicon precursor into the pore structure of the particulate porous frameworks. As used herein, CVI refers to processes in which a gaseous precursor is thermally decomposed on a surface to form elemental silicon at the surface and gaseous by-products. In the case that the precursor is a chlorinated

compound, such as a chlorosilane, the precursor is used in admixture with hydrogen gas, preferably in at least a 1:1 atomic ratio of hydrogen to chlorine.

Optionally, the precursor is free of chlorine. Free of chlorine means that the precursor contains less than 1 wt%, preferably less than 0.1wt%, preferably less than 0.01 wt% of chlorine-containing compounds.

The gaseous silicon precursor may be used either in pure form (or substantially pure form) or as a diluted mixture with an inert carrier gas, such as nitrogen or argon. Preferably step (c) comprises contacting the optimised particulate porous frameworks with a gas comprising at least 30 vol%, or at least 40 vol%, or at least 50 vol%, or at least 60 vol%, or at least 70 vol%, or at least 80 vol%, or at least 90 vol%, or at least 95 vol%, or at least 97 vol%, or at least 99 vol% of the gaseous silicon precursor based on the total volume of the gas.

The presence of oxygen in step (c) should be avoided to prevent undesired oxidation of the deposited electroactive material, in accordance with conventional procedures for working in an inert atmosphere. Preferably, the oxygen content is less than 0.01 vol%, more preferably less than 0.001 vol% based on the total volume of gas used in step (c).

The temperature in step (c) is preferably in the range from 180 to 520 °C, or from 340 to 500 °C, or from 350 to 480 °C, or from 350 to 450 °C, or from 350 to 420 °C, or from 350 to less than 400 °C, or from 355 to 395 °C, or from 360 to 390 °C, or from 360 to 385 °C, or from 360 to 380 °C.

The pressure in step (c) is preferably in the range from 1 to 5000 kPa, or from 20 to 500 kPa, or from 40 to 200 kPa, or from 50 to 150 kPa, or from 60 to 120 kPa, or from 80 to 100 kPa.

Preferably, the pressure in at step (b) is maintained at no more than 200 kPa, or at no more than 150 kPa, or at no more than 120 kPa, or at no more than 110 kPa, or at no more than 100 kPa, or at no more than 90 kPa, or at no more than 80 kPa. References to the pressure in any step of the claimed process refer to the absolute pressure in the reaction zone, which may comprise any suitable form of reactor vessel.

The deposition of electroactive materials by CVI results in the elimination of by-products, particularly by-product gases such as hydrogen. Step (c) preferably further comprises the separation of by-products from the particles formed in step (c). Separation of by-products may be effected by flushing the reactor with an inert gas and/or by evacuating the reactor by reducing the pressure. For example, the separation of by-products from the particles formed in step (c) may be

effected by evacuating the reactor to a pressure of less than 100 kPa, or less than 80 kPa, or less than 60 kPa, or less than 40 kPa, or less than 20 kPa, or less than 10 kPa, or less than 5 kPa, or less than 2 kPa, or less than 1 kPa. Evacuating the reactor to low pressure may be effective not only to remove by-products in the gas phase, but also to desorb any by-products that may be adsorbed onto the surfaces of the deposited silicon.

A range of different silicon loadings in the composite particles may be obtained. The composite particles preferably comprise at least 26 wt% silicon, or at least 28 wt% silicon, or at least 30 wt% silicon, or at least 32 wt% silicon, or at least 34 wt% silicon, or at least 36 wt% silicon, or at least 38 wt% silicon, or at least 40 wt% silicon, or at least 42 wt% silicon, or at least 44 wt% silicon. In any of these cases the composite particles may comprise up to 70 wt% silicon.

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

The amount of silicon in the composite particles can be related to the available pore volume in the optimised particulate porous frameworks by the requirement that the mass ratio of silicon to the optimised particulate porous frameworks is in the range from $[0.5 \times P^1 \text{ to } 1.9 \times P^1] : 1$, wherein P^1 is a dimensionless quantity having the magnitude of the total pore volume of micropores and mesopores in the optimised particulate porous frameworks, as expressed in cm^3/g (e.g. if the optimised particulate porous frameworks have a total volume of micropores and mesopores of $1.2 \text{ cm}^3/\text{g}$, then $P^1 = 1.2$). This relationship takes into account the density of silicon and the pore volume of the optimised particulate porous frameworks to define a weight ratio of silicon at which the pore volume is around 20% to 82% occupied. Preferably, the weight ratio of silicon deposited in step (c) to the optimised particulate porous frameworks is in the range from $[0.6 \times P^1 \text{ to } 1.8 \times P^1] : 1$ or from $[0.7 \times P^1 \text{ to } 1.7 \times P^1] : 1$, or from $[0.8 \times P^1 \text{ to } 1.6 \times P^1] : 1$.

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

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

The internal deposition of the electroactive material is further improved by the requirement that the pressure in step (c) is maintained at less than 200 kPa, or within the more preferred pressure ranges discussed above.

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

It is known in general terms that atoms at the surface of a material have different set of bonding interactions to atoms in the bulk of the material, and this difference is usually described in terms of the surface energy of the material. In the case of silicon that has been deposited by chemical vapor infiltration (CVI), the free valencies of silicon atoms at the surface generally carry hydride groups. If this hydride-terminated silicon surface is accessible to air, it reacts with oxygen to form a native oxide surface. However, surfaces that are not accessible to air remain in the hydride-terminated form.

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

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

Wherein Y is the percentage of surface silicon as a proportion of the total silicon in the sample, $M_{\max}$ is the maximum mass of the sample measured in the temperature range between 550 °C to 650 °C, $M_{\min}$ is the minimum mass of the sample above 150 °C and below 500 °C, and M_f is the mass of the sample at completion of oxidation at 1400 °C. For completeness, it will be understood that 1.875 is the molar mass ratio of SiO_2 to O_2 (i.e. the mass ratio of SiO_2 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 $\pm$ 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 composite particles. Thus, preferably at least 20 wt%, or at least 22 wt%, or at least 25 wt%, or at least 30 wt%, or at least 35 wt % of the silicon of the composite particles is surface silicon as determined by thermogravimetric analysis (TGA). One of the advantages of the invention is that providing the optimised particulate porous frameworks facilitates the achievement of advantageous amounts of surface silicon, when the silicon precursor is used to deposit silicon in the frameworks.

The fact that a significant proportion of hydride-terminated surface silicon is measurable in the particulate material even after passivation in air indicates that the composite particles contain internal silicon surfaces that are inaccessible to air. This indicates that the internal pore spaces of the porous carbon framework are first lined with silicon before being capped to form an internal void space with the hydride-terminated silicon surfaces oriented into the closed internal void space. This in turn indicates that the silicon domains have a characteristic length scale that is much smaller than the pores themselves.

As the internal voids are inaccessible to electrolyte, the silicon surfaces are protected from SEI formation, thereby minimising irreversible lithium loss during the first charge cycle. Additional

exposure of the electroactive material in subsequent charge-discharge cycles is also substantially prevented such that SEI formation is not a significant failure mechanism leading to capacity loss. Simultaneously, this silicon is constrained hydrostatically during lithiation enabling utilization of the voids during lithiation induced expansion.

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In addition to the surface silicon content, the composite particles 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:

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

Wherein Z is the percentage of unoxidized silicon at 800 °C, M_{800} is the mass of the sample at 800 °C, and M_f is the mass of ash at completion of oxidation at 1400 °C. For the purposes of this analysis, it is assumed that any mass increase above 800 °C corresponds to the oxidation of silicon to SiO_2 and that the total mass at completion of oxidation is SiO_2 .

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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.

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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.

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The composite particles preferably have a BET surface area of no more than 300 m^2/g , or no more than 250 m^2/g , or no more than 200 m^2/g , or no more than 150 m^2/g . More preferably, no more than 100 m^2/g , or no more than 80 m^2/g , or no more than 60 m^2/g , or no more than 40 m^2/g , or no more than 30 m^2/g , or no more than 25 m^2/g , or no more than 20 m^2/g , or no more than 15 m^2/g , or no more than 10 m^2/g , or no more than 5 m^2/g . In general, a low BET surface area is preferred to

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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. The BET surface area 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 of the composite particles 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 particle size distribution of the optimised particulate porous frameworks is assumed to be unchanged by the processes which form the composite particles (e.g. step (c)). Accordingly, the particle size distribution parameters defined for the optimised particulate porous frameworks may also be used to define the composite particles (e.g. D₅₀, sphericity, etc.).

In the absence of any indication to the contrary, the pore structure of the composite particles (e.g. pore volume, PD_n pore diameter, etc.) is defined by pore structure of the optimised particulate porous frameworks taken in isolation, i.e. as measured in the absence of any electroactive material (or any other material) occupying the pores of the particulate porous frameworks. Therefore, the pore structure parameters defined for the optimised particulate porous frameworks may also be used to define the composite particles.

When the optimised particulate porous frameworks are optimised particulate porous carbon frameworks, the composite particles may have a ratio of the relative intensity of D and G peaks (I_D/I_G) of ≤2.0 or ≤1.8 as measured by Raman spectroscopy. Alternatively, or in addition, I_D/I_G of the composite particles may be ≥1 or ≥1.05. For example, I_D/I_G of the composite particles may be in the range of 1.0-1.6.

The process may comprise, after step (c), an annealing step of annealing the composite particles at elevated temperature under an inert or reducing atmosphere.

The annealing step is associated with a number of interrelated thermally-induced processes that stabilize the silicon and prolong the cycle-life of the composite particles in LIBs. These processes include elimination of hydrogen from terminal Si-H bonds, volumetric contraction of Si domains resulting in the reopening of some pore space, and the promotion of covalent bonds between silicon and the internal surfaces of the particulate porous frameworks (e.g. Si-C bonds in the case that particulate porous carbon frameworks are used).

For example, the temperature of the annealing step may be at least 450 °C, or at least 500 °C, or at least 510 °C, or at least 520 °C, or at least 540 °C, or at least 560 °C, or at least 580 °C, or at least 600 °C, or at least 610 °C, or at least 620 °C, or at least 630 °C, or at least 640 °C, or at least 650 °C. Preferably, the temperature of the annealing step is no more than 900 °C, or no more than 850 °C, or no more than 800 °C, or no more than 750 °C, or no more than 700 °C, or no more than 680 °C, or no more than 660 °C, or no more than 650 °C.

The temperature of the annealing step may be in the range from 200 °C to 1000 °C, 400 °C to 900 °C, or from 500 °C to 900 °C, or from 600 °C to 900 °C. The temperature of the annealing step may be in the range from 500 °C to 800 °C, or from 510 °C to 800 °C, or from 520 °C to 750 °C, or from 540 °C to 700 °C, or from 560 °C to 680 °C, or from 580 °C to 660 °C, or from 600 °C to 650 °C.

The temperature of the temperature of the annealing step may be greater than the temperature in step (c). Preferably, the temperature of the annealing step is at least 20 °C, or at least 40 °C, or at least 60 °C, or at least 80 °C, or at least 100 °C, or at least 120 °C, or at least 140 °C, or at least 150 °C greater than the temperature in step (c).

The duration of the annealing step is preferably at least 1 minute, or at least 2 minutes, or at least 5 minutes, or at least 10 minutes, or at least 15 minutes, or at least 20 minutes, or at least 30 minutes, or at least 45 minutes, or at least 1 hour, or at least 2 hours. Preferably, the duration of the annealing step is no more than 72 hours, or no more than 48 hours, or no more than 24 hours, or no more than 12 hours, or no more than 6 hours, or no more than 5 hours, or no more than 4 hours, or no more than 3 hours.

The duration of the annealing step may be in the range from 1 minute to 72 hours, or from 2 minutes to 48 hours, or from 5 minutes to 24 hours, or from 10 minutes to 12 hours, or from 15 minutes to 6 hours, or from 20 minutes to 5 hours, or from 30 minutes to 4 hours, or from 1 hour to 4 hours, or from 1 hour to 3 hours.

The annealing step is carried out under an inert or reducing atmosphere. Preferably, the atmosphere is selected from a nitrogen atmosphere, or an atmosphere comprising hydrogen, or a noble gas atmosphere, or mixtures thereof.

Preferably, the annealing step is carried out at a temperature in the range from 400 °C to 900 °C and for a period of from 1 minute to 72 hours. Or at a temperature in the range from 500 °C to 900 °C and for a period of from 30 minutes to 4 hours. Or at a temperature in the range from 600 °C to 900 °C for a period of from 1 hour to 4 hours.

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The ratio of BET surface area of the particles formed after the annealing step to BET surface area of the composite particles may be at least 1.1:1, or at least 1.2:1, or at least 1.3:1, or at least 1.4:1, or at least 1.5:1, or at least 2:1, or at least 3:1, or at least 4:1, or at least 5:1.

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The ratio of BET surface area of the particles formed after the annealing step to BET surface area of the composite particles may be no more than 15:1, or no more than 14:1, or no more than 13:1, or no more than 12:1.

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The ratio of total pore volume of micropores and mesopores as measured by gas adsorption of the particles formed after the annealing step to total pore volume of micropores and mesopores as measured by gas adsorption of the composite particles may be at least 2:1, or at least 3:1, or at least 4:1, or at least 5:1, or at least 6:1, or at least 7:1, or at least 8:1.

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The ratio of total pore volume of micropores and mesopores as measured by gas adsorption of the particles formed after the annealing step to total pore volume of micropores and mesopores as measured by gas adsorption of the composite particles may be no more than 20:1, or no more than 19:1, or no more than 18:1, or no more than 17:1, or no more than 16:1, or no more than 15:1.

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The ratio of total hydrogen content of the particles formed after the annealing step to total hydrogen content of the composite particles may be no more than 0.8:1, or no more than 0.7:1, or no more than 0.6:1, or no more than 0.5:1.

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The ratio of total hydrogen content of the particles formed after the annealing step to total hydrogen content of the composite particles may be at least 0.1:1, or at least 0.2:1, or at least 0.3:1.

The process may comprise, after step (c), a passivating step of contacting the composite particles with a passivating agent.

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As defined herein, a passivating agent is a compound or mixture of compounds which is able to react with the surface of the silicon deposited in step (c) to form a modified surface. In particular, a

passivating agent as defined herein is a material which is able to react with the surfaces of silicon to further reduce the surface energy thereof.

Preferably, the passivating step is carried out after the annealing step. As discussed above, one effect of the annealing step is to reopen pore spaces that were previously obstructed or capped by silicon nanostructures, such that the pore spaces are accessible to passivating gases, thus allowing for a more extensive passivation of the silicon surfaces and the elimination of hydrogen-terminated silicon surfaces.

One type of passivation layer is a native oxide layer. A native oxide layer may be formed, for example, by exposing the silicon surface to a passivating agent selected from air or another oxygen containing gas. The passivation layer may comprise a silicon oxide of the formula SiO_x , wherein $0 < x \leq 2$. The silicon oxide is preferably amorphous silicon oxide. The formation of a native oxide layer is exothermic and therefore requires careful process control to prevent overheating or even combustion of the particulate material. In the case that the passivating agent is an oxygen-containing gas, the passivating step may comprise cooling the composite particles to a temperature below 300 °C, preferably below 200 °C, optionally below 100 °C, prior to contacting with the oxygen-containing gas.

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

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

Other suitable passivating agents include compounds comprising an alkene, alkyne or carbonyl functional group, more preferably a terminal alkene, terminal alkyne, aldehyde or ketone group. Preferred passivating agents include one or more compounds of the formulae:

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

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

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

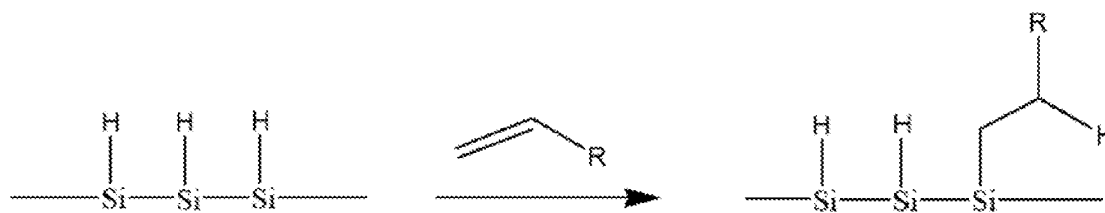
- (i) $\text{CH}_2=\text{CH-R}^1$; and
- (ii) $\text{HC}\equiv\text{C-R}^1$;

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

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

It is believed that passivating agents comprising an alkene, alkyne or carbonyl group undergo an insertion reaction with Si-H groups at the silicon surface to form a covalently passivated surface which is resistant to oxidation by air. The passivation reaction between the silicon surface and the passivating agent may therefore be understood as a form of hydrosilylation, as shown

schematically below.



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

Suitable passivating agents in this category include compounds of the formula

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

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

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

Preferably X represents O or NH .

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

Contacting the composite particles with the passivating agent may be carried out at a temperature in the range of 25 to 500 °C, preferably at a temperature in the range of from 50 to 450 °C, more preferably from 100 to 400 °C.

The process may comprise, after step (c), a depositing step of depositing a lithium-ion permeable material into the pores and/or onto the outer surface of the composite particles. The use of the lithium-ion filler reduces SEI formation by reducing the surface area of the composite particles and by preventing contact between the electrolyte and the silicon domains in the particle interior.

Preferably, the lithium-ion permeable material is a pyrolytic carbon material and the depositing step comprises combining the composite particles with a pyrolytic carbon precursor; and heating the pyrolytic carbon precursor to a temperature effective to cause the deposition of a conductive pyrolytic carbon material into the pores and/or onto the outer surface of the composite particles. In the case that the annealing step is included in the process, the depositing step may optionally be performed before or after the annealing step. If the passivating step is performed, most preferably the depositing step is performed after the passivating step.

The pyrolytic carbon precursor is preferably a hydrocarbon. Suitable hydrocarbons include 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. Suitable pyrolytic carbon precursors also include bicyclic monoterpenoids, optionally wherein the bicyclic monoterpenoid is selected from camphor, borneol, eucalyptol, camphene, careen, sabinene, thujene and pinene. Further suitable pyrolytic carbon precursors include 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. Other suitable pyrolytic carbon precursors include phthalocyanine, sucrose, starches, graphene oxide, reduced graphene oxide, pyrenes, perhydropyrene, triphenylene, tetracene, benzopyrene, perylenes, coronene, and chrysene. A preferred carbon precursor is acetylene.

A suitable temperature for the deposition of a pyrolytic carbon material in the depositing step is in the range from 300 to 800 °C, or from 400 to 700 °C. For example, the temperature may be no more than 680 °C or no more than 660 °C, or no more than 640 °C or no more than 620 °C, or no more than 600 °C, or no more than 580 °C, or no more than 560 °C, or no more than 540 °C, or no more than 520 °C, or no more than 500 °C. The minimum temperature will depend on the type of carbon precursor that is used. Preferably, the temperature is at least 300 °C, or at least 350 °C, or at least 400 °C, or at least 450 °C, or at least 500 °C.

The carbon-containing precursors used in the depositing step may be used in pure form, or as a diluted mixture with an inert carrier gas, such as nitrogen or argon. For instance, the carbon-containing precursor may be used in an amount in the range from 0.1 to 100 vol%, or 0.5 to 20

vol%, or 1 to 10 vol%, or 1 to 5 vol% based on the total volume of the precursor and the inert carrier gas.

In the case that a pyrolytic carbon material is deposited, the same compound may function as both a passivating agent in the passivating step and the pyrolytic carbon precursor in the depositing step. For example, if styrene is selected as the pyrolytic carbon precursor, then it will also function as a passivating agent if the composite particles are not exposed to another passivating agent prior to contact with styrene. In this case, passivation and deposition of the conductive carbon material in steps may be carried out simultaneously, for example at a temperature in the range of from 300-700 °C. Alternatively, passivation and deposition of the conductive carbon material may be carried out sequentially, with the same material as the passivating agent and the pyrolytic carbon precursor, but wherein the depositing step is carried out at a higher temperature than, and following, the passivating step. For example, passivation may be carried out at a temperature in the range of from 25 °C to less than 300 °C, and deposition of pyrolytic carbon may be carried out at a temperature in the range from 300-700 °C. These two steps may suitably be carried out sequentially by increasing the temperature while maintaining contact with the compound that functions as both a passivating agent and the pyrolytic carbon precursor. At lower temperatures (e.g. in the range of 25 °C to <300 °C) passivation will be the primary process. As the temperature is increased (e.g. to 300-700 °C) the deposition of pyrolytic carbon will ensue.

The composite particles may be incorporated into a composition comprising at least one other component. In particular, there is provided a composition comprising the composite particles and at least one other component selected from: (i) a binder; (ii) a conductive additive; and (iii) an additional particulate electroactive material. This composition is useful as an electrode composition, and thus may be used to form the active layer of an electrode.

The composition may be a hybrid electrode composition which comprises the composite particles and at least one additional particulate electroactive material. Examples of additional particulate electroactive materials include graphite, hard carbon, silicon, tin, germanium, aluminium and lead. The at least one additional particulate electroactive material is preferably selected from graphite and hard carbon, and most preferably the at least one additional particulate electroactive material is graphite.

In the case of a hybrid electrode composition, the composition preferably comprises from 3 to 60 wt%, or from 3 to 50 wt%, or from 5 to 50 wt%, or from 10 to 50 wt%, or from 15 to 50 wt%, of the composite particles, based on the total dry weight of the composition. The at least one additional

particulate electroactive material is suitably present in an amount of from 20 to 95 wt%, or from 25 to 90 wt%, or from 30 to 75 wt%, based on the total dry weight of the composition.

5 The at least one additional particulate electroactive material preferably has a D_{50} particle diameter in the range from 10 to 50 μm , preferably from 10 to 40 μm , more preferably from 10 to 30 μm and most preferably from 10 to 25 μm , for example from 15 to 25 μm .

10 The D_{10} particle diameter of the at least one additional particulate electroactive material is preferably at least 5 μm , more preferably at least 6 μm , more preferably at least 7 μm , more preferably at least 8 μm , more preferably at least 9 μm , and still more preferably at least 10 μm .

15 The D_{90} particle diameter of the at least one additional particulate electroactive material is preferably up to 100 μm , more preferably up to 80 μm , more preferably up to 60 μm , more preferably up to 50 μm , and most preferably up to 40 μm .

20 The at least one additional particulate electroactive material is preferably selected from carbon-comprising particles, graphite particles and/or hard carbon particles, wherein the graphite and hard carbon particles have a D_{50} particle diameter in the range from 10 to 50 μm . Still more preferably, the at least one additional particulate electroactive material is selected from graphite particles, wherein the graphite particles have a D_{50} particle diameter in the range from 10 to 50 μm .

25 The composition may also be a non-hybrid (or “high loading”) electrode composition which is substantially free of additional particulate electroactive materials. In this context, the term “substantially free of additional particulate electroactive materials” should be interpreted as meaning that the composition comprises less than 15 wt%, preferably less than 10 wt%, preferably less than 5 wt%, preferably less than 2 wt%, more preferably less than 1 wt%, more preferably less than 0.5 wt% of any additional electroactive materials (i.e. additional materials which are capable of inserting and releasing metal ions during the charging and discharging of a battery), based on the total dry weight of the composition.

30 A “high-loading” electrode composition of this type preferably comprises at least 50 wt%, or at least 60 wt%, or at least 70 wt%, or at least 80 wt%, or at least 90 wt% of the composite particles, based on the total dry weight of the composition.

35 The composition may optionally comprise a binder. A binder functions to adhere the composition to a current collector and to maintain the integrity of the composition. Examples of binders include

polyvinylidene fluoride (PVDF), polyacrylic acid (PAA) and alkali metal salts thereof, modified polyacrylic acid (mPAA) and alkali metal salts thereof, carboxymethylcellulose (CMC), modified carboxymethylcellulose (mCMC), sodium carboxymethylcellulose (Na-CMC), polyvinylalcohol (PVA), alginates and alkali metal salts thereof, styrene-butadiene rubber (SBR) and polyimide.

5 The composition may comprise a mixture of binders. Preferably, the binder comprises polymers selected from polyacrylic acid (PAA) and alkali metal salts thereof, and modified polyacrylic acid (mPAA) and alkali metal salts thereof, SBR and CMC.

10 The binder may suitably be present in an amount of from 0.5 to 20 wt%, preferably 1 to 15 wt%, preferably 2 to 10 wt% and most preferably 5 to 10 wt%, based on the total dry weight of the composition.

15 The binder may optionally be present in combination with one or more additives that modify the properties of the binder, such as cross-linking accelerators, coupling agents and/or adhesive accelerators.

20 The composition may optionally comprise one or more conductive additives. Preferred conductive additives are non-electroactive materials that are included so as to improve electrical conductivity between the electroactive components of the composition and between the electroactive components of the composition and a current collector. The conductive additives may be selected from carbon black, carbon fibers, carbon nanotubes, graphene, acetylene black, ketjen black, metal fibers, metal powders and conductive metal oxides. Preferred conductive additives include carbon black and carbon nanotubes.

25 The one or more conductive additives may suitably be present in a total amount of from 0.5 to 20 wt%, preferably 1 to 15 wt%, preferably 2 to 10 wt% and most preferably 5 to 10 wt%, based on the total dry weight of the composition.

30 The invention also provides an electrode comprising the composite particles and a current collector, wherein the composite particles are in electrical contact with the current collector. The particulate material used to prepare the electrode may be in the form of a composition comprising the composite particles at least one other component defined above.

35 As used herein, the term current collector refers to any conductive substrate that can carry a current to and from the electroactive particles in the composition. Examples of materials that can be used as the current collector include copper, aluminium, stainless steel, nickel, titanium and

sintered carbon. Copper is a preferred material. The current collector is typically in the form of a foil or mesh having a thickness of between 3 to 500 μm . The composite particles may be applied to one or both surfaces of the current collector to a thickness which is preferably in the range from 10 μm to 1 mm, for example from 20 to 500 μm , or from 50 to 200 μm .

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

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Alternatively, the slurry may be formed into a freestanding film or mat comprising the particulate material of the invention, for instance by casting the slurry onto a suitable casting template, removing the solvent and then removing the casting template. The resulting film or mat is in the form of a cohesive, freestanding mass that may then be bonded to a current collector by known methods.

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The electrode may be used as the anode of a metal-ion battery. Thus, the present invention provides a rechargeable metal-ion battery comprising the electrode as the anode. The metal ions are preferably lithium ions. More preferably, the rechargeable metal-ion battery is a lithium-ion battery.

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The cathode of the rechargeable metal-ion battery typically comprises a current collector and a cathode active material capable of releasing and reabsorbing metal ions. The cathode active material is preferably a metal oxide-based composite. Examples of suitable cathode active materials include LiCoO_2 , $\text{LiCo}_{0.99}\text{Al}_{0.01}\text{O}_2$, LiNiO_2 , LiMnO_2 , $\text{LiCo}_{0.5}\text{Ni}_{0.5}\text{O}_2$, $\text{LiCo}_{0.7}\text{Ni}_{0.3}\text{O}_2$, $\text{LiCo}_{0.8}\text{Ni}_{0.2}\text{O}_2$, $\text{LiCo}_{0.82}\text{Ni}_{0.18}\text{O}_2$, $\text{LiCo}_{0.8}\text{Ni}_{0.15}\text{Al}_{0.05}\text{O}_2$, $\text{LiNi}_{0.4}\text{Co}_{0.3}\text{Mn}_{0.3}\text{O}_2$ and $\text{LiNi}_{0.33}\text{Co}_{0.33}\text{Mn}_{0.34}\text{O}_2$.

30

The cathode current collector is generally of a thickness of between 3 to 500 μm . Examples of materials that can be used as the cathode current collector include aluminium, stainless steel, nickel, titanium and sintered carbon.

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Suitable electrolytes for rechargeable metal-ion batteries include a non-aqueous electrolyte containing a lithium salt, and may include, without limitation, non-aqueous electrolytic solutions, organic solid electrolytes, and inorganic solid electrolytes. Examples of non-aqueous electrolyte

solutions that can be used include non-protic organic solvents such as propylene carbonate, ethylene carbonate, butylene carbonates, dimethyl carbonate, diethyl carbonate, gamma butyrolactone, 1,2-dimethoxyethane, 2-methyltetrahydrofuran, dimethylsulfoxide, 1,3-dioxolane, formamide, dimethylformamide, acetonitrile, nitromethane, methylformate, methyl acetate, phosphoric acid triesters, trimethoxymethane, sulfolane, methyl sulfolane and 1,3-dimethyl-2-imidazolidinone.

Examples of organic solid electrolytes include polyethylene derivatives, polyethyleneoxide derivatives, polypropylene oxide derivatives, phosphoric acid ester polymers, polyester sulfide, polyvinylalcohols, polyvinylidene fluoride and polymers containing ionic dissociation groups.

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

The lithium salt is suitably soluble in the chosen solvent or mixture of solvents. Examples of suitable lithium salts include LiCl , LiBr , LiI , LiClO_4 , LiBF_4 , LiBC_4O_8 , LiPF_6 , LiCF_3SO_3 , LiAsF_6 , LiSbF_6 , LiAlCl_4 , $\text{CH}_3\text{SO}_3\text{Li}$ and $\text{CF}_3\text{SO}_3\text{Li}$.

Where the electrolyte is a non-aqueous organic solution, the rechargeable metal-ion battery is preferably provided with a separator interposed between the anode and the cathode. The separator is typically formed of an insulating material having high ion permeability and high mechanical strength. The separator typically has a pore diameter of between 0.01 and 100 μm and a thickness of between 5 and 300 μm . Examples of suitable electrode separators include a micro-porous polyethylene film. The separator may be replaced by a polymer electrolyte material and in such cases the polymer electrolyte material is present within both the composite anode layer and the composite cathode layer. The polymer electrolyte material can be a solid polymer electrolyte or a gel-type polymer electrolyte.

Example 1

Particulate porous carbon frameworks C1 to C16 used in this example have the characteristics set out in Tables 1 and 2.

Table 1

Carbon No.	D ₁₀	D ₅₀	D ₉₀	BET	P ^{1*}	Micropore volume	Feedstock	Activation method
	μm	μm	μm	m ² /g	cm ³ /g	cm ³ /g		
C1	1.3	3.1	7.1	1860	0.80	0.45	Nutshell	Steam
C2	1.8	5.1	9.6	1568	0.69	0.48	Nutshell	Steam
C3	1.7	5.8	10.7	1785	0.79	0.48	Nutshell	Steam
C4	3.2	16.7	41.1	1645	0.70	0.49	Nutshell	Steam
C5	2.2	7.4	15.1	1599	0.73	0.43	Nutshell	Steam
C6	0.9	3.4	8.1	1026	0.59	0.31	Nutshell	Steam
C7	1.8	5.3	10.0	1644	0.77	0.45	Nutshell	Steam
C8	1.8	5.6	10.5	1772	0.77	0.49	Nutshell	Steam
C9	3.7	10.9	25.2	1143	0.53	0.36	Nutshell	Steam
C10	3.2	7.0	13.7	943	0.36	0.33	Phenolic resin	CO ₂
C11	2.1	7.9	18.3	1911	1.29	0.53	Hard wood	H ₃ PO ₄
C12	1.8	4.8	8.5	2493	1.25	0.65	Phenolic resin	KOH
C13	1.2	3.2	7.2	2206	0.93	0.66	Phenolic resin	KOH
C14	2.8	10.0	19.9	1896	0.81	0.49	Phenolic resin	Steam
C15	1.8	4.3	8.1	2004		0.56	Phenolic resin	CO ₂
C16	1.1	2.7	5.4	568		0.23	Phenolic resin	Ethylene glycol template

* P¹ is the total volume of micropores and mesopores

Table 2

Carbon No.	PD ₁₀ /σ [SiH ₄]	PD ₃₀ /σ [SiH ₄]	PD ₅₀ /σ [SiH ₄]	PD ₇₅ /σ [SiH ₄]	PD ₉₀ /σ [SiH ₄]	(PD ₉₀ -PD ₁₀)/σ [SiH ₄]	Average Surface Si / %
C1	1.54	2.06	3.16	6.73	12.29	10.75	33
C2	1.45	1.89	2.43	5.36	12.23	10.77	38
C3	1.30	2.00	2.87	6.01	11.16	9.86	32
C4	1.38	1.91	2.47	5.33	8.72	7.34	28
C5	1.41	2.00	2.93	6.50	14.99	13.58	15
C6	1.35	1.94	3.60	25.22	63.26	61.92	15
C7	1.49	2.04	2.94	6.63	15.33	13.84	18
C8	1.43	2.02	2.85	5.79	8.46	7.03	21
C9	1.45	1.55	2.33	6.21	29.95	28.50	3
C10	1.3	1.43	1.59	2.30	3.54	2.24	0
C11	2.35	3.33	8.66	26.10	46.73	44.38	18
C12	1.96	2.74	4.55	8.03	11.70	9.74	21
C13	1.50	1.89	2.29	5.29	8.51	7.01	23
C14	1.36	2.07	3.14	6.06	7.69	6.34	28
C15	1.52	1.89	2.37	3.78	6.40	4.88	21
C16	2.47	11.87	17.03	26.18	45.40	42.93	11

The particle size and pore structure parameters were measured for the carbon frameworks before deposition of silicon. The total volume of micropores and mesopores and the pore size distribution of micropores and mesopores are determined using nitrogen gas adsorption at 77 K and QSDFT as described herein. Volume-based nth percentile pore diameters PD_n are expressed as a ratio of the pore diameter to the effective size σ for silane (SiH_4), having a value of 0.408 nm.

Silicon-carbon composite particles were prepared by placing about 1.8 g of a particulate porous framework with the properties listed in Tables 1 and 2 on a stainless-steel plate at a constant thickness of 1 mm along its length. The plate was then placed inside a stainless-steel tube of outer diameter 60 mm with gas inlet and outlet lines located in the hot zone of a retort furnace. The furnace tube was purged with nitrogen gas for 30 minutes at room temperature, then the sample temperature was increased to between 450 and 475 °C. The nitrogen gas flow-rate is adjusted to ensure a gas residence time of at least 10 seconds in the furnace tube and maintained at that rate for 30 minutes. Then, the gas supply is switched from nitrogen to a mixture of silane (SiH_4) in nitrogen at 1.25 vol% concentration. Dosing of silane is performed over a period of up to 5-hours with a reactor pressure maintained at 101.3 kPa (1 atm). After dosing has finished the gas flow rate is kept constant whilst the silane is purged from the furnace using nitrogen. The furnace is purged for 30 minutes under nitrogen before being cooled down to room temperature over several hours. The atmosphere is then switched over to air gradually over a period of two hours by switching the gas flow from nitrogen to air from a compressed air supply.

The surface silicon for the composite particles was measured as follows: 10 mg (± 2 mg) of the sample under test was loaded into a 70 μ L crucible. The sample was loaded into a Mettler Toledo TGA/DSC 3+ instrument with an Ar purge gas, N_2 padding gas and air reaction gas at 100 mL/min. The TGA furnace chamber was ramped from 25 to 1400°C at a rate of 10°C/min. Data was collected at 1s intervals. Figure 1 gives TGA plots obtained in this way for the composite particles prepared from C15 and C16. The formula defined above is used to calculate the surface silicon (Y) values.

A series of samples of composite particles were made using each of the carbon frameworks. The average surface silicon was calculated from the TGA curve for each sample and is listed in Table 2. It can be seen that increased average surface silicon is achieved for carbon frameworks having an optimised pore structure for the silicon precursor (SiH_4). In particular, Figures 2-4 show the average surface silicon for the composite particles prepared from each of the porous carbon frameworks plotted vs. a pore structure parameter measured for the framework prior to silicon

deposition. The pore structure parameter is expressed relative to the effective size of SiH₄. Circular datapoints are for frameworks having the optimised pore structure for SiH₄ (C1-C4, C8, C12-C15). Crossed datapoints are for frameworks not having the optimised pore structure for SiH₄ (C5-C7, C9-C11, C16). It can be seen that the composite particles prepared from the frameworks having the optimised pore structure have consistently higher average surface silicon compared to the composite particles prepared from the frameworks not having the optimised pore structure. The inventors have previously shown that high surface silicon levels are associated with improved reversible capacity retention over multiple charge/discharge cycles. Thus, frameworks having an optimised pore structure for a silicon precursor, in this example SiH₄, enable the formation of composite particles with advantageous properties for use as anode electroactive materials for LIBs, when the silicon precursor is used to deposit silicon in the frameworks. It is expected that this effect would be achieved for carbon frameworks having optimised pore structures for alternative silicon precursors.

Example 2

Preparation and characterisation of composite particles

Particulate porous carbon frameworks C17 to C21 used in this example have the characteristics set out in Table 3 and Table 4. Composite particles prepared from these frameworks have the characteristics set out in Table 5.

Table 3

Carbon No.	D ₅₀ μm	BET m ² /g	P ₁ * cm ³ /g	Micropore Volume cm ³ /g	Feedstock	Activation method
C17	3.3	1827	0.76	0.58	Phenolic resin	CO ₂
C18	3.4	1988	0.87	0.60	Phenolic resin	CO ₂
C19	3.3	2051	0.53	0.62	Phenolic resin	CO ₂
C20	4.1	1686	0.39	0.56	Phenolic resin	CO ₂
C21	4.5	716	0.69	0.12	Phenolic resin	No activation

Table 4

Carbon No.	PD ₁₀ /σ [SiH ₄]	PD ₃₀ /σ [SiH ₄]	PD ₅₀ /σ [SiH ₄]	PD ₇₅ /σ [SiH ₄]	PD ₉₀ /σ [SiH ₄]	(PD ₉₀ -PD ₁₀)/σ [SiH ₄]
C17	1.39	1.92	2.80	5.76	7.08	5.69
C18	1.57	2.09	3.47	6.38	7.85	6.28
C19	1.57	2.68	5.56	8.12	11.86	10.29
C20	1.33	1.44	1.92	2.68	9.00	7.67
C21	1.33	21.28	28.02	34.44	48.58	47.25

Table 5

Carbon No.	Surface silicon %	TGA silicon content %
C17	50	50
C18	43	43
C19	64	51
C20	49	37
C21	2	54

The particle size, surface area, and pore structure parameters were measured for the carbon frameworks before deposition of silicon.

5

Silicon-carbon composite particles were prepared using a 0.6L volume pressure reactor system according to the following procedure. Firstly, 25 g of a particulate porous framework with the properties listed in Tables 3 and 4 was weighed and loaded into the reactor chamber, which was then sealed, inerted, and pressure tested using nitrogen gas. The reactor was then heated to a temperature of 320-350°C whilst stirring at 200 rpm. Silane gas was then injected and the furnace set-point increased to 550°C. The silane was injected in four pulses to total 27 g with pressure set point between 9-12 bar on each cycle. Reaction completion at each pulse was determined through pressure monitoring- stabilisation of the pressure was used to determine completion of silane conversion to silicon on the carbon. Following injection of the silane dose, the reactor was inerted once more using nitrogen gas. Subsequently, sixty cycles of passivation using increasing concentrations of air in nitrogen at 150°C until temperature and pressure were stable at 100% air on each injection. These steps grow a passivating layer of silicon dioxide on the outer surface of the composite particles. The resulting composite powder is then reclaimed by breaking the reactor seal and sieving the reclaimed composite powder through a 53 µm sieve.

20

The amount of silicon in the composite particles was determined using TGA. The mass of a sample of composite particles was measured in TGA apparatus in air to completion of oxidation at ~1400 °C. The composite particles are assumed to be formed solely of carbon, silicon, and oxygen. The mass at completion of oxidation is assumed to be solely SiO₂, from which the silicon content of the starting composite particles may be determined. The silicon content determined by TGA for composite particles prepared from each of C17-C21 shows that sufficient silicon was deposited for the composite particles to be used as anode materials for lithium-ion batteries.

25

The surface silicon for the composite particles was measured as follows: 10 mg (±2 mg) of the sample under test was loaded into a 70 µL crucible. The sample was loaded into a Mettler Toledo

30

TGA/DSC 3+ instrument with an Ar purge gas, N₂ padding gas and air reaction gas at 100 mL/min. The TGA furnace chamber was ramped from 25 to 1400°C at a rate of 10°C/min. Data was collected at 1s intervals. The formula defined above is used to calculate the surface silicon (Y) values.

5

Figures 5-7 show the surface silicon for the composite particles prepared from each of the porous carbon frameworks plotted vs. a pore structure parameter measured for the framework prior to silicon deposition. The pore structure parameter is expressed relative to the effective size of SiH₄. Circular datapoints are for frameworks having the optimised pore structure for SiH₄ (C17-C20).

10

Crossed datapoints are for the framework not having the optimised pore structure for SiH₄ (C21). The composite particles prepared from the frameworks having the optimised pore structure have consistently higher surface silicon compared to the composite particles prepared from the framework not having the optimised pore structure.

15

Example 3

Preparation and characterisation of composite particles

Particulate porous carbon frameworks C22 to C28 used in this example have the characteristics set out in Table 6 and Table 7. Composite particles prepared from these frameworks have the characteristics set out in Table 8.

20

Table 6

Carbon No.	D ₅₀ µm	BET m ² /g	P ¹ cm ³ /g	Micropore Volume cm ³ /g	Feedstock	Activation method
C22	3.0	1807	0.73	0.56	Phenolic resin	CO ₂
C23	4.3	1857	0.77	0.52	Phenolic resin	CO ₂
C24	3.3	2129	0.87	0.59	Phenolic resin	CO ₂
C25	3.6	2040	0.86	0.54	Phenolic resin	CO ₂
C26	3.3	1825	0.76	0.46	Phenolic resin	CO ₂
C27	6.6	541	0.71	0.14	Phenolic resin	No activation
C28	6.4	424	0.85	0.10	Phenolic resin	No activation

Table 7

Carbon No.	PD ₁₀ /σ [SiH ₄]	PD ₃₀ /σ [SiH ₄]	PD ₅₀ /σ [SiH ₄]	PD ₇₅ /σ [SiH ₄]	PD ₉₀ /σ [SiH ₄]	(PD ₉₀ -PD ₁₀)/σ [SiH ₄]
C22	1.44	1.63	2.18	3.18	6.17	4.72
C23	1.39	2.00	2.68	5.37	7.32	5.94
C24	1.44	2.00	2.68	5.37	6.61	5.16
C25	1.50	2.00	2.80	5.76	7.32	5.82
C26	1.39	1.92	2.80	5.76	7.08	5.69
C27	1.22	22.04	29.38	34.44	39.52	38.30
C28	2.68	38.20	48.97	59.72	68.53	65.85

Table 8

Carbon No.	Surface silicon	TGA silicon content
	%	%
C22	52	50
C23	59	52
C24	51	55
C25	48	53
C26	50	50
C27	1	53
C28	5	61

- 5 The particle size, surface area, and pore structure parameters were measured for the carbon frameworks before deposition of silicon.

Silicon-carbon composite particles were prepared and characterised using the same procedures as Example 2.

10

Figures 8-10 show the surface silicon for the composite particles prepared from each of the porous carbon frameworks plotted vs. a pore structure parameter measured for the framework prior to silicon deposition. The pore structure parameter is expressed relative to the effective size of SiH₄. Circular datapoints are for frameworks having the optimised pore structure for SiH₄ (C22-C26).

15

Crossed datapoints are for the frameworks not having the optimised pore structure for SiH₄ (C27 and C28). The composite particles prepared from the frameworks having the optimised pore structure have consistently higher surface silicon compared to the composite particles prepared from the frameworks not having the optimised pore structure.

Claims

1. A process comprising the steps of:
 - (a) determining an effective size σ of a silicon precursor;
 - (b) providing a population of optimised particulate porous frameworks comprising
- 5 micropores and/or mesopores and having an optimised pore structure for the silicon precursor, the optimised pore structure comprising:
 - a PD_{30} pore diameter of 1.4σ - 3.0σ ,
 - a PD_{90} pore diameter of 5.0σ - 14.0σ , and
 - a pore diameter span (PD_{90} - PD_{10}) of 4.0σ - 12.0σ ,
- 10 wherein "effective size σ " refers to the value σ in the Lennard-Jones potential for the silicon precursor;
- wherein " PD_n pore diameter" refers to the pore diameter below which $n\%$ of the total micropore and mesopore volume is found.
- 15 2. The process of claim 1, wherein step (b) comprises the steps of:
 - (b1) providing one or more populations of particulate porous frameworks comprising micropores and/or mesopores;
 - (b2) measuring the pore structure of each population;
 - (b3) accepting each population that has the optimised pore structure and rejecting each
- 20 population that does not have the optimised pore structure; and
 - (b4) using one or more of the accepted populations as the population of optimised particulate porous frameworks or, if no populations are accepted, repeating steps (b1), (b2), and (b3) on a further population of particulate porous frameworks comprising micropores and/or mesopores until a population is accepted.
- 25 3. The process of claim 2, wherein at least two populations are provided in step (b1), optionally at least one of which is rejected in step (b3).
4. The process of claim 1, comprising the steps of:
 - 30 (a1) providing one or more silicon precursors;
 - (a2) determining an effective size σ of each silicon precursor;
 - (b5) providing a population of particulate porous frameworks comprising micropores and/or mesopores;
 - (b6) measuring the pore structure of the population;

- (a3) accepting each silicon precursor that has an effective size such that the pore structure is the optimised pore structure for the silicon precursor and rejecting each silicon precursor that has an effective size is such that the pore structure is not the optimised pore structure for the silicon precursor;
- 5 (a4) if no silicon precursors are accepted, repeating steps (a1), (a2), and (a3) on a further silicon precursor until a silicon precursor is accepted.
5. The process of claim 4, wherein at least two silicon precursors are provided in step (a1), optionally at least one of which is rejected in step (a3).
- 10 6. The process of any preceding claim, comprising providing a kit comprising the silicon precursor and the population of optimised particulate porous frameworks.
7. The process of any preceding claim, further comprising providing a further population
- 15 of the optimised particulate porous frameworks at industrial scale; optionally wherein industrial scale means at least 100 kg or at least 1,000 kg.
8. The process of any preceding claim, wherein the optimised pore structure comprises a PD₉₀ pore diameter of 6.0σ - 13.5σ or 8.5σ - 13.0σ .
- 20 9. The process of any preceding claim, wherein the optimised pore structure comprises a pore diameter span (PD₉₀-PD₁₀) of 4.5σ - 11.5σ or 6.0σ - 11.0σ .
10. The process of any preceding claim, wherein the optimised pore structure
- 25 comprises a PD₃₀ pore diameter of 1.6σ - 3.0σ , or 1.7σ - 2.8σ , or 1.8σ - 2.2σ .
11. The process of any preceding claim, wherein the optimised pore structure comprises a PD₅₀ pore diameter of $<4.0\sigma$ or $<3.7\sigma$.
- 30 12. The process of any preceding claim, wherein the optimised pore structure comprises a PD₇₅ pore diameter of 3.75σ - 8.0σ or 5.0σ - 7.0σ .
13. The process of any preceding claim, wherein the particulate porous frameworks are particulate porous carbon frameworks.

35

14. The process of claim 13, wherein the optimised particulate porous carbon frameworks have a ratio of the relative intensity of D and G peaks (I_D/I_G) as measured by Raman spectroscopy of:
≤2.0 or ≤1.8; and/or
5 ≥1 or ≥1.05; and/or
1.0-1.6.
15. The process of claim 13 or 14, comprising chemical or physical activation of a carbonaceous material to provide the particulate porous carbon frameworks comprising
10 micropores and/or mesopores.
16. The process of claim 15, wherein physical activation comprises heating the carbonaceous material in a flow of one or more of oxygen, steam, CO, and CO₂ optionally at a temperature of 600-1200 °C or 600-1000 °C.
15
17. The process of claim 15, wherein chemical activation comprises impregnating the carbonaceous material with a chemical activation agent to form impregnated carbonaceous material, and heating the impregnated carbonaceous material optionally at a temperature of 250-1000 °C or 500-950 °C;
20 optionally wherein the chemical activation agent is selected from NaOH, KOH, K₂CO₃, H₃PO₄, CaCl₂, ZnCl₂, and mixtures thereof.
18. The process of any of claims 15-17, wherein the carbonaceous material is pyrolyzed carbon; optionally pyrolyzed carbon derived from a plant source, or pyrolyzed pitch, or
25 pyrolyzed polymer.
19. The process of claim 13 or 14, wherein providing the particulate porous carbon frameworks comprises providing a carbonaceous material from a plant source, pyrolyzing the carbonaceous material by heating in an inert atmosphere optionally at a
30 temperature of 400 to 900 °C, and contacting the pyrolyzed material with one or more of oxygen, steam, CO, and CO₂ at a temperature in the range from 300 to 1500 °C, or 600 to 1200°C, or 600 to 1000°C.
20. The process of any preceding claim, wherein the silicon precursor in step (a) is a
35 gaseous silicon precursor; optionally wherein the gaseous silicon precursor is selected

- from silane (SiH_4), disilane (Si_2H_6), trisilane (Si_3H_8), tetrasilane (Si_4H_{10}), pentasilane (Si_5H_{12}), hexasilane (Si_6H_{14}), methylsilane (CH_3SiH_3), dimethylsilane ($(\text{CH}_3)_2\text{SiH}_2$), trimethylsilane ($(\text{CH}_3)_3\text{SiH}$), tetramethylsilane ($(\text{CH}_3)_4\text{Si}$), and chlorosilanes such as trichlorosilane (HSiCl_3) or dichlorosilane (H_2SiCl_2) or chlorosilane (H_3SiCl), or
- 5 methylchlorosilanes such as methyltrichlorosilane (CH_3SiCl_3) or dimethyldichlorosilane ($(\text{CH}_3)_2\text{SiCl}_2$).

21. The process of any preceding claim, wherein the effective size σ is a value in the range of 0.4-0.6 nm.

10

22. The process of any preceding claim, wherein the silicon precursor in step (a) is: silane (SiH_4) and the effective size σ is 0.408 nm; or disilane (Si_2H_6) and the effective size σ is 0.483 nm; or trisilane (Si_3H_8) and the effective size σ is 0.556 nm; or

15 trichlorosilane (HSiCl_3) and the effective size σ is 0.564 nm; or dichlorosilane (H_2SiCl_2) and the effective size σ is 0.503 nm; or chlorosilane (H_3SiCl) and the effective size σ is 0.415 nm.

23. The process of any of claims 1-21, wherein the silicon precursor in step (a) is silane

20 (SiH_4) and the effective size σ is 0.408 nm.

24. The process of any of claims 1-21, wherein the silicon precursor in step (a) is disilane (Si_2H_6) and the effective size σ is 0.483 nm.

25 25. The process of any of claims 1-21, wherein the silicon precursor in step (a) is HSiCl_3 and the effective size σ is 0.564 nm.

26. The process of any of claims 1-21, wherein the silicon precursor is not silane (SiH_4), optionally wherein the silicone precursor is not silane (SiH_4) or disilane (Si_2H_6).

30

27. The process of any preceding claim, wherein the optimised pore structure further comprises a micropore volume fraction of at least 0.4 and/or no more than 0.95, based on the total volume of micropores and mesopores.

28. The process of any preceding claim, wherein the optimised pore structure further comprises a total volume of micropores and mesopores as measured by gas adsorption of P^1 cm³/g, wherein P^1 is 0.4-1.8, or 0.5-1.6, or 0.6-1.1.

- 5 29. The process of claim 28, wherein the optimised pore structure further comprises a total volume of pores having a diameter in the range of >50-100 nm of P^2 cm³/g, wherein P^2 is $<0.2 \times P^1$, or $<0.05 \times P^1$, or $<0.005 \times P^1$.

30. The process of any preceding claim, wherein the optimised pore structure further
10 comprises a micropore volume of at least 0.3 cm³/g, or at least 0.4 cm³/g, or at least 0.5 cm³/g, or at least 0.6 cm³/g.

31. The process of any preceding claim, wherein the optimised pore structure further comprises a total volume of pores having a diameter in the range of >50-100 nm of
15 <10%, <5%, or <1% of the total volume of micropores, mesopores, and pores having a diameter in the range of >50-100 nm.

32. The process of any preceding claim, wherein the optimised pore structure further comprises a bimodal or multimodal pore size distribution.

20

33. The process of claim 32, wherein the pore size distribution has peaks in at least two of, optionally in all three of, regions (i), (ii), and (iii):

(i) 1.2σ - 1.7σ ;

(ii) 1.8σ - 2.1σ ; and

- 25 (iii) 2.2σ - 3.2σ .

34. The process of claim 33, wherein peaks (i), (ii), and (iii) include at least the two most intense peaks, optionally the three most intense peaks, in the pore size distribution.

- 30 35. The process of any preceding claim, wherein the optimised particulate porous frameworks have a BET surface area of at least 750 m²/g, or at least 1,000 m²/g, or 1,200-3,000 m²/g.

36. The process of any preceding claim, wherein the optimised particulate porous frameworks have a D_{50} particle diameter of less than 100 μm , or less than 30 μm , or 1-30 μm , or 1-20 μm , or 2-8 μm .

- 5 37. The process of any preceding claim, further comprising the step of:
 (c) contacting the optimised particulate porous frameworks provided by step (b) with the silicon precursor of step (a) at a temperature effective to cause deposition of elemental silicon in the pores of the optimised particulate porous frameworks, thereby providing composite particles.

10

38. The process of claim 37, further comprising the step of:

(d) forming an electrode comprising the composite particles.

39. The process of claim 38, further comprising the step of:

- 15 (e) forming a rechargeable metal-ion battery comprising the electrode.

40. Optimised particulate porous frameworks comprising micropores and/or mesopores and having an optimised pore structure for a silicon precursor, wherein the effective size of the silicon precursor is σ , the optimised pore structure comprising:

- 20 a PD_{30} pore diameter of 1.4σ - 3.0σ ,
 a PD_{90} pore diameter of 5.0σ - 14.0σ , and
 a pore diameter span (PD_{90} - PD_{10}) of 4.0σ - 12.0σ ,

wherein "effective size σ " refers to the value σ in the Lennard-Jones potential for the silicon precursor;

- 25 wherein " PD_n pore diameter" refers to the pore diameter below which $n\%$ of the total micropore and mesopore volume is found.

41. A kit comprising the optimised particulate porous frameworks of claim 40 and the silicon precursor for which the pore structure is optimised.

30

42. Composite particles for use as an electroactive material for a metal-ion battery, the composite particles comprising:

(i) optimised particulate porous frameworks comprising micropores and/or mesopores and having an optimised pore structure for a silicon precursor, wherein the effective size

- 35 of the silicon precursor is σ , the optimised pore structure comprising:

- a PD₃₀ pore diameter of 1.4σ - 3.0σ ,
a PD₉₀ pore diameter of 5.0σ - 14.0σ , and
a pore diameter span (PD₉₀-PD₁₀) of 4.0σ - 12.0σ ,
wherein "effective size σ " refers to the value σ in the Lennard-Jones potential for the
5 silicon precursor;
wherein "PD_n pore diameter" refers to the pore diameter below which n% of the total
micropore and mesopore volume is found; and
(ii) a plurality of elemental silicon domains located within the pores of the optimised
particulate porous frameworks.
10
43. The composite particles of claim 42, wherein at least 20 wt%, or at least 22 wt%, or
at least 25 wt%, or at least 30 wt%, or at least 35 wt% of the silicon is surface silicon as
determined by thermogravimetric analysis (TGA).
15
44. The composite particles of any of claims 42-43, wherein no more than 10 wt%, or no
more than 8 wt%, or no more than 6 wt%, or no more than 5 wt%, or no more than 4
wt%, or no more than 3 wt%, or no more than 2 wt%, or no more than 1.5 wt% of the
silicon is coarse bulk silicon as determined by TGA.
20
45. The composite particles of any of claims 42-44, comprising at least 26 wt%, or at
least 28 wt%, or at least 30 wt%, or at least 32 wt% silicon, or at least 34 wt% silicon, or
at least 36 wt% silicon, or at least 38 wt% silicon, or at least 40 wt% silicon, or at least
42 wt% silicon, or at least 44 wt% silicon.
25
46. An electrode comprising the composite particles of any of claims 42-45.
47. A rechargeable metal-ion battery comprising the electrode of claim 46.