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(54) Title: ANODES WITH POROUS OR MESOPOROUS SILICON PARTICLES

(57) Abstract: The present invention provides anode materials, methods of producing them, electrochemical cells, and lithium-ion batteries, where the anode material comprises (1) mesoporous or porous silicon; and (2) carboxymethyl cellulose. In certain embodiments, the mesoporous or porous silica additionally comprises other materials within its pores, such as lithium.



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## ANODES WITH POROUS OR MESOPOROUS SILICON PARTICLES

[0001] This application claims the priority of U.S. Provisional Application Nos. 61/467,304 and 61/467,308, both filed March 24, 2011; as well as U.S. Non-Provisional Application Nos. 13/429,169 and 13/429,185, both filed March 23, 2012; all four of which are incorporated by reference in their entireties for all purposes.

### BACKGROUND OF THE INVENTION

[0002] There is currently great interest in developing a new generation of heat-stable, nonflammable, high-capacity, long-lived, rechargeable batteries for various applications, including the consumer electronics and automobile industries.

[0003] Conventional lithium ion batteries commonly use carbon anodes. Ding, N. et al. *J. Power Sources* **2009**, 192, 644. Silicon has over ten times the potential capacity to store electrical charge, making it attractive as a possible alternative anode material. *Id.* Unlike carbon, however, silicon will expand by up to 300% or more during battery use. *See id.* Under this mechanical stress, a conventional silicon anode will crack or break apart, reducing the battery's capacity. *Id.*; Kim, H. et al. *Angew. Chem. Int. Ed.* **2008**, 47, 10151. This disadvantage has been a major technical barrier to the creation of higher capacity anodes from silicon. *Id.*

[0004] Attempts to overcome this problem include the use of alternative binders, alternative electrolytes, and alternative anodes, such as carbon coatings on silicon cores, carbon/silicon mixtures (e.g., a silicon dispersion in a carbon matrix), and silicon nanomaterials. *Id.*; Baldwin, R. K. et al. *Chem. Commun.* **2002**, 1822; Lestriez, B. et al. *Electrochem. Commun.* **2007**, 9, 2801; Mazouzi, D. et al. *Electrochem. Solid-State Lett.* **2009**, 12, A215. Anodes made from silicon nanomaterials or nanoparticles can incorporate regular pores, allowing a structure's expansion without damage and loss of capacity. Cho, J. *J. Mater. Chem.* **2010**, 20, 4009. However, silicon nanoparticles can aggregate during battery cycling, which impairs battery performance. No general solution has yet been accepted in the field as optimal.

[0005] Therefore, there is a need to develop mesoporous or porous silicon-based lithium-ion electrochemical cells and batteries that have high thermal stability, excellent durability,

long cycle life, and high charge density. The present invention satisfies these and other needs.

#### BRIEF SUMMARY OF THE INVENTION

[0006] In certain embodiments, the invention presents an anode material comprising:

5 mesoporous or porous silicon particles having an average pore diameter of from about 1 nm to about 500 nm; and carboxymethyl cellulose (CMC). Preferably, the mesoporous or porous silicon particle has a particle diameter from about 50 nm to about 250 nm. More preferably, the particle diameter is from about 80 nm to about 150 nm.

[0007] In another preferred embodiment, the mesoporous or porous silicon particles

10 comprise lithium in the pores. In still another preferred embodiment, the anode material further comprises styrene-butadiene rubber (SBR).

[0008] In certain embodiments, the invention presents a method for preparing an anode material, wherein the method comprises:

15 contacting a silicon tetrahalide with a reducing agent under conditions sufficient to form a reduced silicon;

contacting the reduced silicon with an alkylating agent or an alkoxide to form an alkyl-capped silicon gel;

20 annealing a mixture of the alkyl-capped silicon gel and a template to form a mesoporous silicon particle having an average pore diameter from about 1 nm to about 500 nm;

and mixing the mesoporous silicon particle with carboxymethyl cellulose (CMC), thereby preparing the anode material. Preferably, the average pore diameter is from about 2 nm to about 100 nm, about 2 nm to about 50 nm, or about 10 nm to about 50 nm.

[0009] In certain embodiments, the invention presents a method for preparing an anode material, wherein the method comprises:

25 contacting a silicon tetrahalide with a reducing agent under conditions sufficient to form a reduced silicon;

contacting the reduced silicon with an alkylating agent or an alkoxide to form an alkyl-capped silicon gel;

30 drying the alkyl-capped silicon gel;

contacting the dried, alkyl-capped silicon gel with hydrofluoric acid to form porous silicon particles having an average pore diameter from about 1 to about 500 nm; and

mixing the porous silicon particle with carboxymethyl cellulose (CMC), thereby preparing the anode material.

[0010] Preferably, the silicon tetrahalide is silicon tetrachloride. Preferably, the reducing agent is sodium naphthalide. Preferably, the alkylating agent is alkyl lithium. In another preferred embodiment, the alkylating agent comprises a C<sub>1-6</sub> alkyl group. Preferably, the template is a nanoparticle template consisting of, consisting essentially of, or comprising silica or alumina.

[0011] In another preferred embodiment, the method further comprises heating the alkyl-capped silicon gel to remove the reducing agent. In still another preferred embodiment, the method further comprises removing the template before the mixing step.

[0012] In certain embodiments, the invention presents an anode material prepared by a method described herein. Preferably, before the mesoporous or porous silicon mixing step with CMC, the method further comprises a step of depositing lithium in a silicon particle pore to form a lithiated mesoporous or porous silicon particle.

[0013] In certain embodiments, the invention presents a lithium-ion battery (i.e., Li-ion battery) prepared by a method described herein. Preferably, before the mesoporous or porous silicon and CMC mixing step, the method further comprises a step of depositing lithium in a silicon particle pore to form a lithiated mesoporous or porous silicon particle.

[0014] In certain other embodiments, the invention presents a lithium-ion battery (i.e., Li-ion battery) prepared by a method described herein.

[0015] These and other aspects, objects, and advantages will become more apparent when read with the following detailed description and drawings.

## DETAILED DESCRIPTION OF THE INVENTION

### I. Definitions

[0016] The terms “a,” “an,” or “the” as used herein not only include aspects with one member, but also include aspects with more than one member. For example, an embodiment of a method including the step “contacting a silicon tetrahalide with a reducing agent” should be understood to present certain aspects with two or more silicon tetrahalides, two or more reducing agents, or both.

[0017] “About” as used herein applies to a defined range around a numerical value. When “X” is a numerical value, “about X,” generally indicates a value from 0.95X to 1.05X. Any reference to “about X” specifically indicates at least the values X, 0.95X, 0.96X, 0.97X, 0.98X, 0.99X, 1.01X, 1.02X, 1.03X, 1.04X, and 1.05X. Thus, “about X” is intended to imply and provide written description support for a claim limitation of, *e.g.*, “0.98X.” However, when the quantity measured in “X” only includes whole integer values (*e.g.*, “X carbons”), “about X” indicates from (X-1) to (X+1). In this case, “about X” as used herein specifically indicates at least the values X, X-1, and X+1. When “about” is applied to the beginning of a numerical range, it applies to both ends of the range. Thus, “from about 5 to 20%” is equivalent to “from about 5% to about 20%” (and vice versa). When “about” is applied to the first value of a set of values, it applies to all values in that set. Thus, “about 7, 9, or 11%” is equivalent to “about 7%, about 9%, or about 11%.”

[0018] The term “alkyl” as used herein, whether by itself or as part of another substituent, includes a straight- or branched-chain hydrocarbon radical having the number of carbon atoms designated (*i.e.*, C<sub>1-8</sub> means one to eight carbons). Examples of alkyl groups include methyl, ethyl, n-propyl, isopropyl, n-butyl, t-butyl, isobutyl, sec-butyl, n-pentyl, n-hexyl, n-heptyl, n-octyl, and the like. When a prefix is not included to indicate the number of chain carbon atoms in an alkyl portion, the radical or portion thereof will have 20 or fewer chain carbon atoms.

[0019] The term “alkylating agent” as used herein includes a reagent that will form a bond between an alkyl group and a particular substrate, typically by the nucleophilic displacement of a leaving group. Examples of alkylating agents include alkyl lithiums (*e.g.*, methyl lithium, butyl lithium) or alkyl magnesium reagents (*e.g.*, Grignard reagents). Those of skill in the art will know of other alkylating agents suitable for use in the present invention.

[0020] The term “alkoxide” as used herein includes RO<sup>-</sup>, where R is an alkyl group as defined herein. Generally, the anionic alkoxide has an associated cation X, which preferably is a metal ion (*e.g.*, sodium, lithium, or potassium). Examples of alkoxide groups include methoxide, ethoxide, t-butoxide, and the like. Those of skill in the art will know of other alkoxides suitable for use in the present invention.

[0021] The terms “halo” or “halogen,” by themselves or as parts of another substituent, includes a fluorine, chlorine, bromine, or iodine atom. “Halide” as used herein refers to the anion of a halogen (*e.g.*, fluoride for fluorine).

[0022] The term “ionic liquid” means a salt comprising a cation and an anion. The salt is a liquid at ambient or near ambient temperatures. Preferably, the cations are organic cations.

[0023] The term “mesoporous” as used herein includes a porous material in which at least some of the pores are regularly arranged. For example, a honeycomb-like structure would be mesoporous, as would a porous structure that included at least 10%, 20%, 35%, 50%, 75% or 90% regularly arranged pores (e.g., a particle with some irregularly arranged pores and some regularly arranged pores). In certain embodiments, a mesoporous material has an average pore size from about 2 to 50 nm, about 1 to 100 nm, or about 2 to 200 nm.

[0024] The term “or” as used herein should in general be construed non-exclusively. For example, an embodiment of “a battery comprising the anode material A or B” would typically present an aspect with the battery comprising both A and B. “Or” should, however, be construed to exclude those aspects presented that cannot be combined, e.g., without contradiction.

[0025] Generally, when a percentage range is taught, it incorporates all full or partial percentages in between (*i.e.*, within the bounds of the range). For example, a percentage range of 15 to 25% would also teach *inter alia* the specific values of 17.36% and 21%. A percentage range of about 13 to 17% would also teach *inter alia* the specific values of 12.97%, 16%, and 17.1%.

[0026] The term “negative electrode” as used herein includes one of a pair of rechargeable lithium-ion cell electrodes that under normal circumstances and when the cell is fully charged will have the lowest potential. This terminology is retained to refer to the same physical electrode under all cell operating conditions even if such electrode is temporarily (e.g., due to cell overdischarge) driven to or exhibits a potential above that of the other (the positive) electrode.

[0027] The term “porous” as used herein includes a material with at least one pore (*i.e.*, a hole or opening). In certain embodiments, a pore allows passage of a fluid (e.g., gas- or liquid-phase molecules) through the surface of the material in which the pore is situated. A pore may be, but is not necessarily, linked to a second opening in a material’s surface.

[0028] The term “positive electrode” as used herein includes one of a pair of rechargeable lithium-ion cell electrodes that under normal circumstances and when the cell is fully charged will have the highest potential. This terminology is retained to refer to the same physical electrode under all cell operating conditions even if such electrode temporarily (e.g., due to

cell overdischarge) is driven to or exhibits a potential below that of the other (the negative) electrode.

## II. Anode Material

[0029] In certain embodiments, the present invention provides an anode material

5 comprising mesoporous or porous silicon particles having an average pore diameter from about 1 nm to about 500 nm. Preferably, the pore diameter is from about 10 nm to about 400 nm, about 25 nm to about 325 nm, about 50 nm to about 250 nm, or about 60 nm to about 200 nm. Preferably, the mesoporous or porous silicon particle has a pore diameter from about 70 nm to about 175 nm, about 80 nm to about 150 nm, or about 90 nm to about 125  
10 nm. In certain embodiments, the pore diameter is from 2 nm to about 50 nm, about 2 nm to about 40 nm, about 2 nm to about 25 nm, about 5 nm to about 50 nm, about 5 nm to about 30 nm, about 10 nm to about 50 nm, about 20 nm to about 75 nm, about 25 nm to about 100 nm, about 50 nm to about 150 nm, or about 100 nm to about 200 nm. In certain embodiments, the pore diameter is from about 100 nm to about 250 nm, about 125 nm to about 250 nm, about  
15 150 nm to about 300 nm, about 100 nm to about 400 nm, or about 250 nm to about 500 nm.

[0030] In certain embodiments, the present invention provides an anode material

comprising mesoporous or porous silicon particles with a particle diameter of from about 50 nm to about 250 nm, about 60 nm to about 200 nm, about 70 nm to about 175 nm, about 80 nm to about 150 nm, or about 90 nm to about 125 nm. In certain embodiments, the particle  
20 diameter is from about 25 nm to about 75 nm, about 35 nm to about 100 nm, about 50 nm to about 150 nm, or about 100 nm to about 200 nm. In certain embodiments, the particle diameter is from about 125 nm to about 200 nm, about 125 nm to about 250 nm, about 150 nm to about 300 nm, about 100 nm to about 400 nm, or about 250 nm to about 500 nm. Preferably, the mesoporous or porous silicon particles have an average particle diameter of  
25 about 200 nm or less. Without intending to be bound by a particular theory, smaller particle sizes are believed to provide a greater density of silicon, thereby producing better anode properties (e.g., more robust; higher capacity).

[0031] In certain embodiments, the present invention provides an anode material

comprising carboxymethyl cellulose (CMC). Although not intending to be constrained by  
30 theory, the CMC is believed to act as a binder for the silicon particles. In certain embodiments, the binder consists or consists essentially of CMC. In certain other embodiments, the binder further comprises other binding agents, such as styrene-butadiene rubber (SBR), poly(ethylene-co-acrylic acid) (PEAA), poly(vinyl pyrrolidone) (PVP),

poly(vinylidene fluoride) (PVDF), other substituted anionic alkyl celluloses, and the like. Preferably, the binder further comprises SBR. In certain embodiments, the binder further comprises binding agents with low elongation at break, such as polyacrylic acid (PAA) and its salts (e.g., K-, Li- or Na-PAA), polyimide, alginate and the like. Preferably, the binder  
5 further comprises PAA or alginate.

[0032] In certain embodiments, the present invention provides an anode material substantially free from PVDF. PVDF is used as a binder for both the positive and negative electrodes in commercial lithium-ion batteries. However, current methods for use of PVDF involve toxic, volatile organic compounds (e.g., the VDF monomer). Embodiments of the  
10 invention that are substantially free from PVDF present the additional advantage of a more environmentally friendly material. In certain embodiments, “substantially free from PVDF” indicates a detectable level of PVDF or VDF that is at most about 1%, 0.8%, 0.5%, 0.3%, or 0.1%. In certain embodiments, “substantially free” indicates a detectable level of PVDF or VDF that is at most about 0.08%, 0.05%, 0.03%, or 0.01%. In certain embodiments,  
15 “substantially free” indicates a detectable level of PVDF or VDF that is at most about 0.008%, 0.005%, 0.003%, or 0.001%. In certain embodiments, “substantially free” indicates a detectable level of PVDF or VDF that is at most about 0.0008%, 0.0005%, 0.0003%, or 0.0001%. In certain preferred embodiments, “substantially free from PVDF” indicates free from detectable PVDF or VDF.

### 20 III. Method of Making

[0033] In certain embodiments, the present invention provides a method for making mesoporous or porous silicon particles that comprises contacting a silicon tetrahalide with a reducing agent under conditions sufficient to form a halide-capped silicon. This silicon is then reacted with a capping group, such as an alkylating agent or an alkoxide.

25 [0034] In certain preferred embodiments, the method has further steps. In certain embodiments, to create the three-dimensional mesoporous or porous silicon structure, the resulting silicon material is mixed with a template and annealed under an inert gas, such as argon. The template is then removed from the mesoporous or porous silicon (e.g., by etching).

30 [0035] In certain embodiments, to create the three-dimensional porous or macroporous silicon structure, the resulting silicon material is dried and contacted with a silicon-dissolving reagent such as hydrofluoric acid. In certain embodiments, the concentration of silicon-dissolving reagent used is about 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.1, 1.2, 1.3, 1.4, 1.5, 1.6, 1.7, 1.8,

1.9, or 2.0 M. In certain embodiments, the etching time is about 10 min, 15 min, 20 min, 25 min, 30 min, 40 min, 45 min, 50 min, 1.0 hour, 1.1 hour, 1.25 hours, 1.5 house, 1.75 hours, 2 hours, 2.25 hours, 2.5 hours, 2.75 hours, 3.0 hours, 3.25 hours, 3.5 hours, 3.75 hours, 4.0 hours, 4.25 hours, 4.5 hours, 4.75 hours, or 5 hours.

5 [0036] In certain embodiments, the method comprises contacting a silicon tetrahalide. The silicon tetrahalide can comprise fluoride, chloride, bromide, iodide, or a mixture of halides (e.g., silicon dichloride dibromide). Preferably, the silicon tetrahalide is silicon tetrachloride or tetrabromide. More preferably, the silicon tetrahalide is silicon tetrachloride.

[0037] In certain embodiments, the method comprises contacting a reducing agent.

10 Preferably, the reducing agent is sodium naphthalide. Other reducing agents include alkali and alkali earth metals such as lithium, sodium, potassium, zinc, and the like.

[0038] In certain embodiments, the present invention provides a method for making mesoporous or porous silicon particles that comprises contacting the reduced silicon with an alkylating agent or an alkoxide to form a capped silicon gel. Differing capping groups and  
15 annealing temperatures may influence the carbon layer's properties. Without intending to be bound by a particular theory, this capping group is believed to create a thin carbon layer that helps to prevent particle aggregation, to prevent silicon dioxide formation, and to stabilize the solid-electrolyte interface (SEI).

[0039] In certain embodiments, the method comprises an alkylating agent (i.e., as described  
20 above, a reactant causing a substrate to form a product with a new bond to an alkyl group). Preferably, the alkylating agent comprises a C<sub>1-6</sub> alkyl group; more preferably, a C<sub>2-3</sub> alkyl group. Preferably, the alkylating agent includes a nucleophilic alkyl group, such as alkyl lithium (e.g., methyl lithium, butyl lithium) or alkyl magnesium reagents (e.g., Grignard reagents). Other possible alkyl group sources include alkyl copper reagents, acetylides,  
25 cyanide, and the like.

[0040] In certain embodiments, the method comprises an alkoxide. Preferably, the alkoxide comprises a C<sub>1-6</sub> alkyl group; more preferably, a C<sub>2-3</sub> alkyl group. Suitable alkoxides include those derived from the alcohols methanol, ethanol, propanol, isopropanol, butanol, and 2-butanol. Suitable alkoxides can also be derived from diols, such as ethylene  
30 glycol and 1,3-propanediol.

[0041] In certain embodiments, the method comprises heating the capped silica silicon to remove the reducing agent or to anneal the gel. Preferably, the capped silica silicon (or,

alternatively, the oven interior or other heating vessel containing the capped silica silicon) is heated to about 100 °C, 110 °C, 120 °C, 130°C, 140 °C, 150 °C, 175 °C, or 200 °C to remove the reducing agent. Preferably, the capped silica silicon (or, alternatively, the oven interior or other heating vessel containing the capped silica silicon) is heated to about 500 °C, 600 °C,  
5 700 °C, 800°C, 850°C, 900 °C, 950 °C, 1000 °C, 1100 °C, or 1200 °C to anneal the gel.

**[0042]** In certain embodiments, the method comprises heating the capped silicon to remove the reducing agent or to dry the gel. Preferably, the capped silicon (or, alternatively, the oven interior or other heating vessel containing the capped silicon) is heated to about 100 °C, 110 °C, 120 °C, 130°C, 140 °C, 150 °C, 175 °C, or 200 °C to remove the reducing agent.

10 Preferably, the capped silicon (or, alternatively, the oven interior or other heating vessel containing the capped silicon) is heated to about 40 °C, 600 °C, 80 °C, 100°C, 125 °C, 150 °C, 175 °C, or 200 °C to dry the gel. Preferably, the capped silicon is heated for 1, 2, 4, 8, 14, or 24 hr for drying.

**[0043]** In certain embodiments, the macroporous or porous silica is created by using  
15 templates. In a preferred embodiment, the template is sized to make pores with an average pore diameter within a preferred range as previously described. Preferably, the template comprises silica or alumina. Preferably, the template has an about 20, 40, 50, 60, 70, 80, 90, 100, 125, 150, 175, 200, 250 , or 300 nm particle size. Preferably, the resulting silica pores are symmetrical in shape, not irregular. Preferably, each pore forms part of a larger pattern  
20 (e.g., domains of a substantially periodic structure similar to a honeycomb).

**[0044]** In a preferred embodiment, the template is removed by etching. Preferably, a chemical etching agent, such as hydrofluoric acid or a solution of hydrofluoric acid, is used for etching. In some embodiments, the concentration of the etching agent is about 0.05, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.1, 1.2, 1.3, 1.4, or 1.5 M. In certain embodiments,  
25 the concentration of etching agent used is about 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.1, 1.2, 1.3, 1.4, 1.5, 1.6, 1.7, 1.8, 1.9, or 2.0 M. In certain embodiments, the etching time is about 10 min, 15 min, 20 min, 25 min, 30 min, 40 min, 45 min, 50 min, 1.0 hour, 1.1 hour, 1.25 hours, 1.5 house, 1.75 hours, 2 hours, 2.25 hours, 2.5 hours, 2.75 hours, 3.0 hours, 3.25 hours, 3.5 hours, 3.75 hours, 4.0 hours, 4.25 hours, 4.5 hours, 4.75 hours, or 5 hours.

30 **[0045]** In certain embodiments, no template is used. Preferably, the pores are created by direct etching with hydrofluoric acid or a solution of hydrofluoric acid. Pore diameters and pore wall thicknesses are controlled by varying the duration and concentration of the

hydrofluoric acid etching. Advantageously, this can minimize contamination of the surface with silicon dioxide, which can decrease battery capacity.

[0046] In a preferred embodiment, the CMC is added to the macroporous silica in a slurry. Preferably, the slurry comprises water. Preferably, the slurry's pH is modified to increase the contact between the CMC and the macroporous silica; more preferably, the slurry's pH is acidic and adjusted to 3.5.

[0047] In certain embodiments, the present invention provides a method for making mesoporous or porous silicon particles that further comprising depositing a metal (e.g., an alkali metal, such as lithium) into the pore before the mixing step to form a metal-containing (e.g., lithiated) mesoporous or porous silicon particle. Preferably, the metal is deposited by a method of chemical vapor deposition.

[0048] In certain embodiments, the porous or mesoporous silicon particles (or, alternatively, the oven interior or other heating vessel containing the capped silicon) is heated to about 500 °C, 600 °C, 700 °C, 800°C, 850°C, 900 °C, 950 °C, 1000 °C, 1100 °C, or 1200 °C to anneal the gel.

#### IV. Lithium Ion Batteries

[0049] In one aspect, the present invention sets forth an electrochemical cell that includes (i) a positive electrode comprising a positive electrode material and a positive electrode current collector; wherein the positive electrode material is in electronically conductive contact with the positive electrode current collector; (ii) a negative electrode comprising a negative electrode material and a negative electrode current collector; wherein the negative electrode material is in electronically conductive contact with the negative electrode current collector; and (iii) an ion conductive medium comprising an ion conductive layer and an electrolyte solution in ionically conductive contact with the positive electrode and the negative electrode. *See, e.g.*, US 2010/0285352 A1; PCT/US2009/045723; WO 2009/148971; U.S. Patent Application No. 12/953,335.

[0050] Preferably, the electrochemical cell further comprises at least one positive electrode tab having a first attachment end and a second attachment end, wherein the first attachment end is connected to the positive electrode current collector. Preferably, the positive electrode comprises LiCoO<sub>2</sub>, LiNi/Co/AlO<sub>2</sub>, LiFePO<sub>4</sub>, or LiNi/Co/MnO<sub>2</sub> mixed oxides. In some embodiments, the positive electrode comprises LiMn<sub>2</sub>O<sub>4</sub> or high-voltage spinel. Preferably, the positive electrode current collector is a conductive sheet selected from the group consisting of a sheet, a fiber sheet, a foam, a nanotube film, a nanofilm, and a mixture

thereof, each of which has an in-plane electrical conductivity of at least about 1000 S/cm. More preferably, the in-plane electrical conductivity is at least about 1100 S/cm, 1200 S/cm, 1300 S/cm, 1400 S/cm, 1500 S/cm, 1750 S/cm, or 2000 S/cm.

**[0051]** Preferably, the electrochemical cell further comprises at least one negative electrode tab having a first attachment end and a second attachment end, wherein the first attachment end is connected to the negative electrode current collector; and wherein the tabs are made from an electrically conductive material, such as a metal, a metal alloy or a composite material. In one embodiment, the metal is selected from the group consisting of copper, nickel, chromium, aluminum, titanium, stainless steel, gold, tantalum, niobium, hafnium, zirconium, vanadium, indium, cobalt, tungsten, beryllium and molybdenum and alloys thereof or an alloy thereof.

**[0052]** In certain instances, the tab has protective coatings against corrosion. The coatings can be any of the above metals, anodizing and oxide coatings, conductive carbon, epoxy and glues, paints and other protective coatings. In other instances, the coatings can be nickel, silver, gold, palladium, platinum, rhodium or combinations thereof for improving conductivity of the tabs. The alloys can be a combination of metals described herein or formed by combining the metals described above with other suitable metals known to persons of skill in the art.

**[0053]** In certain instances, the electrolyte solution comprises  $\text{LiPF}_6$ .

**[0054]** In certain instances, the electrolyte solution comprises a lithium compound and a solvent selected from an ionic liquid of formula (I) or a mixture of an organic solvent and an ionic liquid of formula (I):



$\text{Q}^+$  is a cation selected from the group consisting of dialkylammonium, trialkylammonium, tetraalkylammonium, dialkylphosphonium, trialkylphosphonium, tetraalkylphosphonium, trialkylsulfonium,  $(\text{R}^f)_4\text{N}^+$  and an N-alkyl or N-hydrogen cation of a 5- or 6-membered heterocycloalkyl or heteroaryl ring having from 1-3 heteroatoms as ring members selected from N, O or S, wherein the heterocycloalkyl or heteroaryl ring is optionally substituted with from 1-5 optionally substituted alkyls and  $\text{R}^f$  is alkyl or alkoxyalkyl.  $\text{E}^-$  is an anion selected from the group consisting of  $\text{R}^1\text{-X-R}^2(\text{R}^3)_m$ ,  $\text{NC-S}^-$ ,  $\text{BF}_4^-$ ,  $\text{PF}_6^-$ ,  $\text{R}^a\text{SO}_3^-$ ,  $\text{R}^a\text{PF}_3$ ,  $\text{R}^a\text{CO}_2^-$ ,  $\text{I}^-$ ,  $\text{ClO}_4^-$ ,  $(\text{FSO}_2)_2\text{N-}$ ,  $\text{AsF}_6^-$ ,  $\text{SO}_4^-$ ,  $\text{B}^-(\text{OR}^d)_2(\text{OR}^e)_2$  and bis[oxalate(2-)-O,O']borate. The subscript m is 0 or 1. X is N when m is 0. X is C when m is 1.  $\text{R}^1$ ,  $\text{R}^2$  and  $\text{R}^3$  are each

independently an electron-withdrawing group selected from the group consisting of halogen, -CN, -SO<sub>2</sub>R<sup>b</sup>, -SO<sub>2</sub>-L<sup>a</sup>-SO<sub>2</sub>N<sup>+</sup>Li<sup>+</sup>SO<sub>2</sub>R<sup>b</sup>, -P(O)(OR<sup>b</sup>)<sub>2</sub>, -P(O)(R<sup>b</sup>)<sub>2</sub>, -CO<sub>2</sub>R<sup>b</sup>, -C(O)R<sup>b</sup> and -H, with the proviso that R<sup>1</sup> and R<sup>2</sup> are other than hydrogen when m = 0, and no more than one of R<sup>1</sup>, R<sup>2</sup> and R<sup>3</sup> is hydrogen when m = 1. Each R<sup>a</sup> is independently C<sub>1-8</sub> perfluoroalkyl. L<sup>a</sup> is C<sub>1-4</sub> perfluoroalkylene. Each R<sup>b</sup> is independently selected from the group consisting of C<sub>1-8</sub> alkyl, C<sub>1-8</sub> haloalkyl, C<sub>1-8</sub> perfluoroalkyl, perfluorophenyl, aryl, optionally substituted barbituric acid and optionally substituted thiobarbituric acid. At least one carbon-carbon bond of the alkyl or perfluoroalkyl are optionally substituted with a member selected from -O- or -S- to form an ether or a thioether linkage and the aryl is optionally substituted with from 1-5 members selected from the group consisting of halogen, C<sub>1-4</sub>haloalkyl, C<sub>1-4</sub>perfluoroalkyl, -CN, -SO<sub>2</sub>R<sup>c</sup>, -P(O)(OR<sup>c</sup>)<sub>2</sub>, -P(O)(R<sup>c</sup>)<sub>2</sub>, -CO<sub>2</sub>R<sup>c</sup> and -C(O)R<sup>c</sup>, wherein R<sup>c</sup> is independently C<sub>1-8</sub> alkyl, C<sub>1-8</sub> perfluoroalkyl or perfluorophenyl and L<sup>a</sup> is C<sub>1-4</sub>perfluoroalkylene. R<sup>d</sup> and R<sup>e</sup> are each independently an alkyl group. In one embodiment, two R<sup>d</sup> groups together with the oxygen atoms to which the two R<sup>d</sup> groups are attached and the boron atom to which the oxygen atoms are attached form a five- or six-member ring, which is optionally fused with a six-membered aromatic ring having 0-1 nitrogen heteroatom, and optionally two R<sup>e</sup> groups together with the oxygen atoms to which the two R<sup>d</sup> groups are attached and the boron atom to which the oxygen atoms are attached form a five- or six-member ring, which is optionally fused with a six-membered aromatic ring having 0-1 nitrogen heteroatom. In some embodiments, at least one positive electrode tab having a first attachment end and a second attachment end, wherein the first attachment end is connected to the positive electrode current collector; optionally, at least one negative electrode tab having a first attachment end and a second attachment end, wherein the first attachment end is connected to the negative electrode current collector.

**[0055]** In another aspect, the present invention provides a battery. The battery includes a housing, a positive connector, a negative connector, an electrochemical cell disposed in the housing, where the positive and the negative connector are mounted on the housing. In one embodiment, the housing is a sealed container.

**[0056]** In another aspect, the present invention provides a battery pack. The battery pack includes a plurality of cells, wherein each cell comprises an ionic liquid of formula (I):



wherein Q<sup>+</sup> is a cation selected from the group consisting of dialkylammonium, trialkylammonium, tetraalkylammonium, dialkylphosphonium, trialkylphosphonium,

tetraalkylphosphonium, trialkylsulfonium,  $(R^f)_4N^+$  and an N-alkyl or N-hydrogen cation of a 5- or 6-membered heterocycloalkyl or heteroaryl ring having from 1-3 heteroatoms as ring members selected from N, O or S, wherein the heterocycloalkyl or heteroaryl ring is optionally substituted with from 1-5 optionally substituted alkyls and each  $R^f$  is

- 5 independently alkyl or alkoxyalkyl.  $E^-$  is an anion selected from the group consisting of  $R^1-XR^2(R^3)_m$ ,  $NC-S^-$ ,  $BF_4^-$ ,  $PF_6^-$ ,  $R^aSO_3^-$ ,  $R^aPF_3$ ,  $R^aCO_2^-$ ,  $I^-$ ,  $ClO_4^-$ ,  $(FSO_2)_2N^-$ ,  $AsF_6^-$ ,  $SO_4^-$  and bis[oxalate(2-)-O,O']borate, wherein m is 0 or 1. X is N when m is 0. X is C when m is 1.  $R^1$ ,  $R^2$  and  $R^3$  are each independently an electron-withdrawing group selected from the group consisting of halogen, -CN,  $-SO_2R^b$ ,  $-SO_2-L^a-SO_2N^+Li^+SO_2R^b$ ,  $-P(O)(OR^b)_2$ ,  $-P(O)(R^b)_2$ , -  
 10  $CO_2R^b$ ,  $-C(O)R^b$  and -H; with the proviso that  $R^1$  and  $R^2$  are other than hydrogen when m = 0, and no more than one of  $R^1$ ,  $R^2$  and  $R^3$  is hydrogen when m = 1. Each  $R^a$  is independently  $C_{1-8}$  perfluoroalkyl. Each  $R^b$  is independently selected from the group consisting of  $C_{1-8}$  alkyl,  $C_{1-8}$  haloalkyl,  $C_{1-8}$  perfluoroalkyl, perfluorophenyl, aryl, optionally substituted barbituric acid, and optionally substituted thiobarbituric acid. At least one carbon-carbon  
 15 bond of the alkyl or perfluoroalkyl are optionally substituted with a member selected from -O- or -S- to form an ether or a thioether linkage and the aryl is optionally substituted with from 1-5 members selected from the group consisting of halogen,  $C_{1-4}$ haloalkyl,  $C_{1-4}$ perfluoroalkyl, -CN,  $-SO_2R^c$ ,  $-P(O)(OR^c)_2$ ,  $-P(O)(R^c)_2$ ,  $-CO_2R^c$  and  $-C(O)R^c$ , wherein  $R^c$  is independently  $C_{1-8}$  alkyl,  $C_{1-8}$  perfluoroalkyl or perfluorophenyl and  $L^a$  is  
 20  $C_{1-4}$ perfluoroalkylene.

[0057] As background, this patent incorporates by reference the teachings of U.S. Patent Nos. 4,830,940; 5,472,808; 5,529,859; 5,571,635; 5,639,577; 6,019,802; 6,203,947; 6,261,722; 6,679,846; 6,506,524; 6,699,623; 6,780,541; and 6,790,243.

## 25 V. Examples

[0058] Example 1: Synthesis of Mesoporous Silicon

- [0059] The first steps are conducted in a glove box under an argon atmosphere. Sodium naphthalide solution is prepared by mixing sodium metal with naphthalene in 1,2-dimethoxyethane (DME) solvent for two hours. A solution of silicon tetrachloride in DME is  
 30 added, and the combination is mixed overnight. Alkyl lithium (e.g., methyl lithium) is then added to the solution and mixed overnight to terminate the silicon atoms by an alkyl group.

[0060] The solution is taken out of the glove box to retrieve the alkyl-capped silicon gel. The DME is removed by evaporation using a rotary evaporator. The resulting gel is then

heated at 130 °C in a vacuum oven (i.e., the oven temperature was 130 °C) for 8 h to remove naphthalene. The resulting powder is extracted with hexane, and the organic phase is washed six times with water in an extraction funnel to remove sodium and lithium chloride.

[0061] The alkyl capped silicon is mixed with a spherical nanoparticles silica template (80 nm particle size) and annealed at 900 °C under argon for three hours. The resulting mesoporous, carbon-coated silicon is mixed with a hydrofluoric acid solution to dissolve the silica template. The mixture is filtered. After the solids are washed with water and alcohol, the silicon product is dried under vacuum at 100 °C for six hours.

[0062] Example 2: Synthesis of Mesoporous Silicon II

[0063] The first steps are conducted in a glove box under an argon atmosphere. Sodium naphthalide solution is prepared by mixing sodium metal with naphthalene in 1,2-dimethoxyethane (DME) solvent for two hours. A solution of silicon tetrachloride in DME is added, and the combination is poured into a Hastelloy Parr reactor. A vacuum is applied to the reactor so that the pressure is between 150 mTorr and 1 Torr. The temperature of the reactor is adjusted between 200°C and 400°C. The reaction time varies between 2 hours to 24 hours. After the reaction, the reactor is opened, and alkyl lithium (e.g., methyl lithium) is then added to the solution and mixed overnight to terminate the silicon atoms by an alkyl group.

[0064] The solution is taken out of the glove box to retrieve the alkyl-capped silicon gel. The DME is removed by evaporation using a rotary evaporator. The resulting gel is then heated at 130 °C in a vacuum oven (i.e., the oven temperature was 130 °C) for 8 h to remove naphthalene. The resulting powder is extracted with hexane, and the organic phase is washed six times with water in an extraction funnel to remove sodium and lithium chloride.

[0065] The alkyl capped silicon is mixed with a spherical nanoparticles silica template (80 nm particle size) and annealed at 900 °C under argon for three hours. The resulting mesoporous, carbon-coated silicon is mixed with a hydrofluoric acid solution to dissolve the silica template. The mixture is filtered. After the solids are washed with water and alcohol, the silicon product is dried under vacuum at 100 °C for six hours.

[0066] Example 3: Synthesis of Porous Silicon

[0067] The first steps are conducted in a glove box under an argon atmosphere. Sodium naphthalide solution is prepared by mixing sodium metal with naphthalene in 1,2-dimethoxyethane (DME) solvent for two hours. A solution of silicon tetrachloride in DME is

added, and the combination is mixed overnight. Alkyl lithium (e.g., methyl lithium) is then added to the solution and mixed overnight to terminate the silicon atoms by an alkyl group.

[0068] The solution is taken out of the glove box to retrieve the alkyl-capped silicon gel.

The DME is removed by evaporation using a rotary evaporator. The resulting gel is then

5 heated at 130 °C in a vacuum oven (i.e., the oven temperature was 130 °C) for 8 h to remove naphthalene. The resulting powder is extracted with hexane, and the organic phase is washed six times with water in an extraction funnel to remove sodium and lithium chloride. The powder is then dried at 100 °C in a vacuum oven (i.e., the oven temperature was 200 °C) for at least six hours.

10 [0069] The dried, alkyl-capped silicon is then mixed with a dilute hydrofluoric acid solution to form pores on the surface of the silicon. Depending on the pore characteristics required, the concentration of hydrofluoric acid used is from 0.5 to 2 M, and the etching time is from 30 min to 5 hours. The mixture is filtered. After the solids are washed with water and alcohol, the silicon product is dried under vacuum at 100 °C for six hours.

15 [0070] Example 4: Synthesis of Porous Silicon II

[0071] The first steps are conducted in a glove box under an argon atmosphere. Sodium naphthalide solution is prepared by mixing sodium metal with naphthalene in 1,2-

dimethoxyethane (DME) solvent for two hours. A solution of silicon tetrachloride in DME is added, and the combination is poured into a Hastelloy Parr reactor. A vacuum is applied to

20 the reactor so that the pressure is between 150 mTorr and 1 Torr. The temperature of the reactor is adjusted between 200°C and 400°C. The reaction time varies between 2 hours to 24 hours. After the reaction, the reactor is opened, and alkyl lithium (e.g., methyl lithium) is then added to the solution and mixed overnight to terminate the silicon atoms by an alkyl group.

25 [0072] The solution is taken out of the glove box to retrieve the alkyl-capped silicon gel.

The DME is removed by evaporation using a rotary evaporator. The resulting gel is then

heated at 130 °C in a vacuum oven (i.e., the oven temperature was 130 °C) for 8 h to remove naphthalene. The resulting powder is extracted with hexane, and the organic phase is washed six times with water in an extraction funnel to remove sodium and lithium chloride.

30 [0073] The dried, alkyl-capped silicon is then mixed with a dilute hydrofluoric acid solution to form pores on the surface of the silicon. Depending on the pore characteristics required, the concentration of hydrofluoric acid used is from 0.5 to 2 M, and the etching time

is from 30 min to 5 hours. The mixture is filtered. After the solids are washed with water and alcohol, the silicon product is dried under vacuum at 100 °C for six hours.

[0074] Optionally, the alkyl capped silicon is then annealed at 900 °C under argon for three hours. The annealed products are washed with water and alcohol, and the silicon product is  
5 dried under vacuum at 100 °C for six hours.

[0075] All publications and patent applications cited in this specification are herein incorporated by reference as if each individual publication or patent application were specifically and individually incorporated by reference. This includes the two U.S.  
10 provisional applications that are identified by attorney docket numbers 026951-001600US (entitled “Anodes with Mesoporous Silicon Particles”) and 026951-001700US (entitled “Anodes of Porous Silicon Particles”). It also includes the U.S. non-provisional applications that are identified by attorney docket numbers 91328-834245-001610US (entitled “Anodes with Mesoporous Silicon Particles”) and 91328-834246-001710US (entitled “Anodes of  
15 Porous Silicon Particles”).

[0076] Although sample embodiments of the foregoing invention have been described in some detail, it will be readily apparent to those of ordinary skill in the art that in light of the teachings of this invention, certain changes and modifications may be made thereto without departing from the spirit or scope of the appended claims.

1 WHAT IS CLAIMED IS:

2           1.     An anode material comprising:  
3           mesoporous silicon particles having an average pore diameter from about 1  
4 nm to about 500 nm; and  
5           carboxymethyl cellulose (CMC).

1           2.     An anode material comprising:  
2           porous silicon particles having an average pore diameter of from about 1 to  
3 about 500 nm; and  
4           carboxymethyl cellulose (CMC).

1           3.     The anode material of claim 1 or 2, wherein the mesoporous silicon  
2 particle has a particle diameter of from about 50 nm to about 250 nm.

1           4.     The anode material of claim 1 or 2, wherein the mesoporous silicon  
2 particle has a particle diameter from about 80 nm to about 150 nm.

1           5.     The anode material of claim 1 or 2, wherein the silicon particles  
2 comprise lithium in the pores.

1           6.     The anode material of claim 1 or 2, further comprising styrene-  
2 butadiene rubber (SBR).

1           7.     A method for preparing the anode material of claim 1, comprising:  
2           contacting a silicon tetrahalide with a reducing agent under conditions  
3 sufficient to form a reduced silicon;  
4           contacting the reduced silicon with an alkylating agent or an alkoxide to form  
5 an alkyl-capped silicon gel;  
6           annealing a mixture of the alkyl-capped silicon gel and a template to form a  
7 mesoporous silicon particle having an average pore diameter from about 1 nm to about 500  
8 nm; and  
9           mixing the mesoporous silicon particle with carboxymethyl cellulose (CMC),  
10 thereby preparing the anode material of claim 1.

1           8.     The method of claim 7, wherein the silicon tetrahalide is silicon  
2 tetrachloride.

- 1                   **9.**       The method of claim 7, wherein the reducing agent is sodium  
2 naphthalide.
- 1                   **10.**     The method of claim 7, wherein the alkylating agent is alkyl lithium.
- 1                   **11.**     The method of claim 7, wherein the alkylating agent comprises a C<sub>1-6</sub>  
2 alkyl group.
- 1                   **12.**     The method of claim 7, wherein the template is a nanoparticle silica  
2 template.
- 1                   **13.**     The method of claim 7, further comprising heating the alkyl-capped  
2 silicon gel to remove the reducing agent.
- 1                   **14.**     The method of claim 7, further comprising before the mixing step,  
2 removing the template.
- 1                   **15.**     The method of claim 7, further comprising before the mixing step,  
2 depositing lithium in the pore to form a lithiated mesoporous silicon particle.
- 1                   **16.**     The method of claim 15, wherein the depositing is performed via  
2 chemical vapor deposition (CVD).
- 1                   **17.**     An anode material prepared by the method of claim 7.
- 1                   **18.**     An anode material prepared by the method of claim 15.
- 1                   **19.**     A method for preparing the anode material of claim 2, comprising:  
2                   contacting a silicon tetrahalide with a reducing agent under conditions  
3 sufficient to form a reduced silicon;  
4                   contacting the reduced silicon with an alkylating agent or an alkoxide to form  
5 an alkyl-capped silicon gel;  
6                   drying the alkyl-capped silicon gel;  
7                   contacting the dried, alkyl-capped silicon gel with hydrofluoric acid to form  
8 porous silicon particles having an average pore diameter from about 1 to about 500 nm; and  
9                   mixing the porous silicon particle with carboxymethyl cellulose (CMC),  
10 thereby preparing the anode material of claim 2.

- 1                   **20.**     The method of claim **19**, wherein the silicon tetrahalide is silicon  
2     tetrachloride.
- 1                   **21.**     The method of claim **19**, wherein the reducing agent is sodium  
2     naphthalide.
- 1                   **22.**     The method of claim **19**, wherein the alkylating agent is alkyl lithium.
- 1                   **23.**     The method of claim **19**, wherein the alkylating agent comprises a  
2     C<sub>1-6</sub> alkyl.
- 1                   **24.**     The method of claim **19**, further comprising heating the alkyl-capped  
2     silicon gel to remove the reducing agent.
- 1                   **25.**     An anode material prepared by the method of claim **19**.
- 1                   **26.**     A Li-ion battery comprising the anode material of claim **1** or **2**
- 1                   **27.**     Use of mesoporous silicon particles and carboxymethyl cellulose for  
2     an anode material, wherein the silicon particles have an average pore diameter from about 1  
3     nm to about 500 nm.
- 1                   **28.**     Use of porous silicon particles and carboxymethyl cellulose for an  
2     anode material, wherein the silicon particles have an average pore diameter from about 1 nm  
3     to about 500 nm.