



(12) **DEMANDE DE BREVET CANADIEN**
CANADIAN PATENT APPLICATION

(13) **A1**

(22) Date de dépôt/Filing Date: 2021/04/30

(41) Mise à la disp. pub./Open to Public Insp.: 2021/07/08

(30) Priorité/Priority: 2020/04/30 (US63/017,837)

(51) Cl.Int./Int.Cl. *H01M 4/134* (2010.01),
H01M 10/0525 (2010.01), *H01M 4/1395* (2010.01),
H01M 4/62 (2006.01)

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(54) Titre : PROCEDE DE FORMATION D'ANODES DE SILICIUM

(54) Title: METHOD FOR FORMING SILICON ANODES

(57) Abrégé/Abstract:

A nano-porous Si particle is produced by providing a quantity of metallurgical silicon, depositing a quantity of a metal on the surface of the quantity of metallurgical silicon to produce a metal deposited metallurgical silicon, etching the metal deposited metallurgical silicon and depositing a ceramic layer on the etched metal deposited metallurgical silicon. The nano-porous Si particle may be formed into an anode and/or incorporated into in a battery.

ABSTRACT

5 A nano-porous Si particle is produced by providing a quantity of metallurgical silicon, depositing a quantity of a metal on the surface of the quantity of metallurgical silicon to produce a metal deposited metallurgical silicon, etching the metal deposited metallurgical silicon and depositing a ceramic layer on the etched metal deposited metallurgical silicon. The nano-porous Si particle may be formed into an anode and/or incorporated into in a battery.

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METHOD FOR FORMING SILICON ANODES

BACKGROUND

1. Technical Field

5 This disclosure relates generally to batteries and in particular to method for forming silicon anodes.

2. Description of Related Art

10 Lithium ion batteries are one of the most important energy storage technologies, for much of the world's energy storage market ranging from the consumer electronics to electric vehicles or distributed energy storage systems. The increasing demands from end users have stimulated the development of lithium ion batteries with higher energy and power density, better rate capacity, and longer cycling life.

15 Silicon (Si) has been long considered as the most promising anode alternative for use in lithium ion batteries due to its high theoretical capacity, moderate working voltage and large abundance on the earth. Despite significant advances, Si-based anodes still face great problems towards practical applications. One problem is the lack of a scalable and low-cost fabrication method for nanostructured Si. Current fabrication methods have not adequately addressed a cost-effective way to reduce the cost of Si anode, due to the process complexity and/or high-cost starting materials. For example, chemical vapor deposition is able to deposit Si nanoparticles with
20 less than **100** nm, but requires high temperature and expensive precursors (such as Si₂H₆, SiH₄). On the other hand, top-down approaches are mostly based on high-cost electronic-grade Si (n-type, p-type, boron-doped, purity > **99.99999%**) as feedstock, and involve the use of template or lithography steps that increases process complexity. Another problem is that most Si
25 anodes reported so far are based on half cells (Li metal as counter electrode), and the use of excess Li metal in half cells "shield" the efficiency and cycling problems of Si anode. It is challenging to assess their feasibility in full cells which are required in practical applications.
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SUMMARY OF THE DISCLOSURE

According to a first embodiment, there is disclosed a method for producing an anode for a battery comprising providing a quantity of metallurgical silicon, etching the metal deposited metallurgical silicon and depositing a ceramic layer on the etched metal deposited metallurgical silicon. The method may further comprise depositing a quantity of a metal on the surface of the quantity of metallurgical silicon to produce a metal deposited metallurgical silicon before etching.

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The method may further comprise reducing the size of the metallurgical silicon into particles having a diameter selected to be between **0.5** and **50** mm. The reducing may comprise mechanically reducing. The mechanical reducing may comprise crushing.

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The metal may be selected from the group comprising silver, gold, platinum, nickel and iron. The metallurgical silicon may be immersed in a solution containing a salt of the metal. The metal may be deposited on to the surface of the metallurgical silicon through a galvanic displacement reaction.

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The ceramic layer may comprise a metal oxide. The metal oxide may be selected from the group consisting of aluminum oxide, titanium oxide, zirconium oxide and silicon oxide. The ceramic layer may comprise a metal oxynitride. The metal oxynitride is selected from the group consisting of aluminium oxynitride, titanium oxynitride and tantalum oxynitride.

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The ceramic layer may be selected to have a thickness between **1** and **20** nm. The ceramic layer may be formed by atomic layer deposition.

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According to a further embodiment, there is disclosed an anode for a battery comprising at least one particle of porous metallurgical silicon having a ceramic layer formed thereover.

The particle of porous metallurgical silicon may be formed by metal assisted chemical etching a quantity of metallurgical silicon. The ceramic layer may be formed by atomic layer deposition. The ceramic layer may be selected to have a thickness of between **1** and **20** nm. A plurality of particles of porous metallurgical silicon may be secured in a binder.

According to a further embodiment, there is disclosed a lithium ion battery comprising a cathode, an anode comprising at least one particle of porous metallurgical silicon having a ceramic layer formed thereover and a non-aqueous lithium containing electrolyte between the cathode and anode.

Other aspects and features of the present disclosure will become apparent to those ordinarily skilled in the art upon review of the following description of specific embodiments in conjunction with the accompanying figures.

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BRIEF DESCRIPTION OF THE DRAWINGS

The accompanying drawings constitute part of the disclosure. Each drawing illustrates exemplary aspects wherein similar characters of reference denote corresponding parts in each view,

20 Figure 1 is a flowchart illustrating one exemplary process of the present disclosure.

Figure 2 depicts a quantity of metallurgical silicon for use in the exemplary process of the present disclosure.

25 Figure 3 depicts a plurality of particles of mechanically reduced metallurgical silicon in accordance with the exemplary process of the present disclosure.

Figure 4 depicts a cleaned plurality of particles of mechanically reduced metallurgical silicon in accordance with the exemplary process of the present disclosure.

30 Figure 5 is an image of the surface of a particle deposited with a metal in accordance with the exemplary process of the present disclosure.

Figure 6 is an image of the etched surface of the particle of Figure 5 in accordance with the exemplary process of the present disclosure.

Figures 7A-F are images of the surface of the during the exemplary process of the present disclosure.

Figure 8A-8D are graphs illustrating the cycling performance of batteries utilizing an anode produced using exemplary processes of the present disclosure.

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DETAILED DESCRIPTION

Aspects of the present disclosure are now described with reference to exemplary apparatuses, methods and systems. Referring to Figure 1, an exemplary process for forming nano-porous silicon (Si) according to a first embodiment is shown generally at 10. In particular, the present method provides a cost-effective route to obtain nano-porous Si particles by scalable metal-assisted chemical etching (MCE) procedure using inexpensive metallurgical silicon and further introducing of an ultrathin ceramic or other protective layer deposited by atomic layer deposition (ALD) to stabilize the Si anode surface. The combination of the nano-porous structure and nanoscale ALD coating layer can not only benefit for the electrolyte filtration but also accommodate large mechanical strains during the lithium insertion and extraction processes, thus leading to a significant improvement in electrochemical performance.

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As illustrated in Figure 1, the present method 10 utilizes a quantity of metallurgical silicon 8 as an initial material. It will be appreciated that metallurgical silicon is commonly formed by reducing naturally occurring silica to silicon however not to a purity level typically required for electronics production. The metallurgical silicon 8 is then mechanically reduced in size to a particle size between 0.5 and 50 mm in step 12. In practice it has been found for use in battery anode production a size of approximately 5 mm has been useful. The size reduction of the metallurgical silicon may be accomplished by any known means and in particular may be performed by mechanical reduction including crushing. Thereafter in step 14, the size reduced metallurgical silicon is cleaned so as to provide a clean surface for subsequent steps. In particular, the size-reduced metallurgical silicon may be

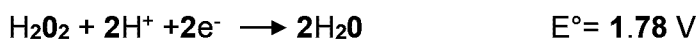
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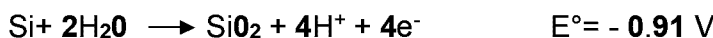
degreased in known degreasing compositions including acetone and isopropyl, water sulphuric acid, hydrogen peroxide and the like.

5 The cleaned metallurgical silicon particles then have nanoparticles of a metal deposited on the surface thereof in step **16**. In particular, the metallic deposition may be accomplished by known methods including immersion in a solution of the metallic salt and deposition on the surface by a galvanic displacement reaction although it will be appreciated that other methods, such as, by way of non-limiting example, physical vapour deposition could also be
10 utilized. In the present disclosure, the metal utilized is silver (Ag) although it will be appreciated that other metals may also be utilized, such as, by way of non-limiting example, gold, platinum, nickel or iron. After the application of metal particles, the surface of the particles may again be optionally cleaned or rinsed in step **18** to remove any residual metal or other materials.

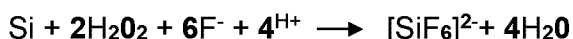
15 The metal deposited metallurgical silicon may then be etched by any suitable means in step **20**. In particular, the etching may be performed in a suitable acid, such as, by way of non-limiting example, hydrofluoric acid and hydrogen peroxide. Alternatively the etching may be performed using other means
20 including without limitation electrochemical etching without the addition of the metal particles. The working principle of chemical etching is based on a local oxidation of the Si surface by a metal catalyst and H_2O_2 , and the subsequent dissolution of silicon oxide in an HF solution. In this galvanic reaction, metal Ag nanoparticles act as a local cathode and a catalyst to promote the
25 reduction of H_2O_2 and produce free holes at the interface of Ag and Si, while the Si surface serves as anode. On the anode, the Si is dissolved continuously by transferring electrons to the Ag particles at the interface of Ag and Si in order to reduce H_2O_2 to H_2O . At the cathode, Ag particles are oxidized into Ag^+ ions by H_2O_2 , and the Ag^+ ions are reduced to Ag by
30 accepting electrons from Si. With this repeated procedure, the Si underneath the Ag particles is continuously etched down to make porous structures. The cathode, anode and total chemical reactions can be listed as the following:
Cathode:



Anode:



5 Totals:



For the total reaction, the standard potential is **2.69 V**, indicating that the etching process is highly thermodynamically favored.

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In step **22**, the residual nano particles may then be removed from the etched metallurgical silicon surface through the use of a suitable rinsing agent, such as water nitric acid or the like depending upon the metal used and optional mechanical agitation with ultrasonics or the like. The etched and cleaned metallurgical silicon particles then have a layer of a ceramic applied thereto through the use of atomic layer deposition or the like in step **24**. In particular the protective coating layer deposited in step **24** may be selected to be a metal oxide, such as, by way of non-limiting example, Aluminum Oxide (Al_2O_3), titanium dioxide (TiO_2), zirconium oxide (ZrO_2) or silicon oxide (SiO_2) or a metal oxynitride, such as, by way of non-limiting example, aluminium oxynitride (AlON), titanium oxynitride (TiO_xN_y) or tantalum oxynitride (TaON). It will be appreciated that the thickness of this layer may be varied depending on the size of the particles and the intended use of the coated particles and in particular for use in a lithium ion battery anode may be selected to be between **1** and **20** nm thick.

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It will be appreciated that the process of the present disclosure provides a cost-effective route to obtain nano-porous Si particles using a scalable metal-assisted chemical etching procedure from inexpensive metallurgical silicon and further introducing of an ultrathin ceramic coating to stabilize the Si anode surface. The combination of the nano-porous structure and nanoscale ceramic coating layer may provide benefits for the electrolyte filtration but also accommodates large mechanical strains during the lithium insertion and

extraction processes, thus leading to a significant improvement in electrochemical performance. The etched and coated particles may subsequently be mixed into a binder and applied to a current collector to form an anode for use in a battery.

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Example 1

A massive metallurgical silicon (-5 cm) was firstly mechanical crushed into small particles (-5 mm) for later treatment.

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Surface clean: the surface of metallurgical silicon particles was thoroughly washed by the following procedure. Firstly, the metallurgical silicon was degreased in acetone and isopropanol for **30** min, rinsed with deionized (DI) water. Secondly, they were cleaned in a piranha solution (**3:1** concentrated H_2SO_4 /**30%** H_2O_2) for **15** min at room temperature followed by rinsing by DI water.

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Ag deposition: the metallurgical silicon particle with clean surface was immersed into the solution of **10** mM AgNO_3 and **5** M HF for the Ag nanoparticles deposition. Ag nanoparticles were deposited onto the surface of Si via a galvanic displacement reaction. Subsequently, excess silver precursors were completely removed by rinsing several times with DI water.

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Metal-assisted chemical etching: the Ag-deposited Si were immersed into an etchant consisting of **10M** HF and **0.5M** H_2O_2 at **50** °C for **3** h for the etching reaction. After the etching process, the Si particles were rinsed with concentrated HNO_3 and large amount of DI water to remove any residual Ag nanoparticles. The nano-porous Si samples (Etched metallurgical silicon) were obtained by intensive ultrasonication.

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ALD Al_2O_3 deposition: an ultrathin Al_2O_3 coating was obtained at **100** °C by alternatively supplying trimethylamine (TMA) and H_2O into a commercial ALD reactor (GEMStar™ XT Atomic Layer Deposition System) with **30** ALD cycles.

Example 2

PEALD metal nitride deposition: In an alternative method, metal nitrides (AlN, TiN) coating on the as-prepared etched metallic silicon are performed in a plasma-enhanced ALD system (PLEAD). ALD-AlN is deposited at temperatures of **100°C - 150 °C** by using trimethylamine (TMA) and plasma N₂ gas (**99.999%**) as precursors. ALD-TiN is deposited at temperatures of **100°C - 150 °C** by using tetrakis(dimethylamido)titanium (TDMAT) and plasma N₂ gas (**99.999%**) as precursors. TiN has a higher electronic conductivity than ceramics (such as Al₂O₃). The use of TD MAT, rather than TiCl₄, as Ti precursor was found to be advantageous for achieving uniform and high-quality TiN thin film.

Example 3

PEALD metal oxynitride deposition: In an alternative method, Titanium oxynitride (TiON) is deposited on the as-prepared etched metallic silicon at **150°C** by combining ALD TiO₂ and TiN deposition cycles in the PEALD system. TiO₂ is deposited by alternatively introducing TD MAT and plasma O₂, while TiN is deposited by using TDMAT and plasma N₂. The composition of TiON is controlled by adjusting the subcycle ratio of TiO₂ and TiN (**2:1, 1:1, 1:2**) in order to tailor the electronic conductivity of titanium oxynitride thin film. The coating of TiON is directly applied on the as-prepared etched metallic silicon.

The morphology and element mapping were observed by using scanning electron microscope (SEM) equipped with energy-dispersive X-ray spectroscopy (EDX). Images of the scanned surface are illustrated in Figure 7A through 7I. In particular Figure 7A illustrates the resultant particles after Ag deposition, Figure 7B illustrates the particles after etching and Figure 7C illustrates the particles after sonication.

As can be seen from Figure 7a, there shows a homogenous Ag nanoparticles deposition on the surface of Si particles via a galvanic displacement reaction. The deposited Ag nanoparticles will act as an important role in the following

chemical reaction process in HF-H₂O₂ system. As illustrated in Figures 7b and 7c, an obvious porous structure was observed at the surface of the Si. Figures 7d, 7d-1 and 7d-2 show the elements mapping after etching and the corresponding mapping of Si and Ag, indicating a certain amount of residual Ag existing on the surface. After being treated in concentrated HNO₃, as shown in Figures 7e, 7e-1 and 7f there is no Ag signal mapping can be detected any more, meaning that the successful removal of residual Ag. Finally, the nano porous Si with high purity was obtained as displayed in Figure 7l.

Electrochemical measurements of the etched and coated porous metallurgical silicon were performed using two-electrode coin cells assembled in an argon filled glove box. For preparing the working electrode, 60 wt% Etched metallurgical silicon@ALD-Al₂O₃ active material, 30 wt% Super P conductive agent, and 10 wt% poly(vinylidene fluoride) binder were mixed in N-methyl-2-pyrrolidone to form a slurry which was applied onto a copper foil current collector using doctor-blade technique and then dried under vacuum at 80 °C overnight. After that, the electrode was cut into round disks ($\phi=12$ mm) for the testing electrode in coin cells. The mass loading was around 2.0 mg on each disk. Electrochemical tests were carried out using CR2032 coin cells assembled in a glove box filled Ar gas with high purity. Li metal foil was used as the counter electrode and polypropylene (PP) (Celgard 2500) as the separator. 1.3 M LiPF₆ in a 3:7 ethylene carbonate: diethyl carbonate (EC: DEC) with 10% fluoroethylene carbonate (FEC) additive were used as electrolyte and each cell was filled with 80 μ L electrolyte. The cells were galvanostatically charged and discharged in a voltage window of 0.05-1.0 V (vs. Li⁺/Li) at different current densities on a Neware BTS 4000 battery tester. The charge/discharge specific capacities were calculated based on the mass of active materials. All the electrochemical testing was conducted at room temperature (20 °C).

For comparison, a metallurgical silicon powder, which was prepared from metallurgical particles through ball-milling, was also tested as LIB anodes.

The metallurgical silicon powder, etched metallurgical silicon and etched and coated metallurgical silicon were galvanostatically cycling at **0.3C (1C=2000 mA g⁻¹)** in the voltage window of **0.05-1.0 V**. As shown in Figure 8A, the metallurgical silicon powder only shows a discharge capacity of less than **20** 5 **mAh g⁻¹** for all the cycles, indicating a non-electrochemical activity for the raw metallurgical silicon materials. As expected, the etched metallurgical silicon shows a dramatic capacity increase after the etching which demonstrating the adopted MCE method can have great effectiveness in producing highly-electrochemical active Si. The etched metallurgical silicon delivers an initial 10 discharge and charge capacities of **3036.1 mAh g⁻¹** and **2120.6 mAh g⁻¹**, respectively, with a Coulombic efficiency of **69.8%**. With additional ALD Al₂O₃ coating, the etched and coated metallurgical silicon exhibits an initial discharge capacity of **3099.1 mAh g⁻¹** and a charge capacity of **2265.7 mAh g⁻¹**, indicating a Coulombic efficiency of **73.1 %**. The improved efficiency of the 15 etched and coated metallurgical silicon (**73.1%**) in the first cycle compared to that of the etched metallurgical silicon (**69.9%**) should be associated with the ALD Al₂O₃ coating layer, which decrease side reactions between the Si and electrolyte, and expedites the formation of the stable solid/electrolyte interface (SEI) layer on the surface of Si. Furthermore, Figures 8A and 8C shows 20 clearly that the etched and coated metallurgical silicon displays much better cycling stability and higher capacities than the etched metallurgical silicon. The discharge capacity of the etched metallurgical silicon changes from **3036.1 mAh g⁻¹** in the initial cycle to **395.7 mAh g⁻¹** in the **1001st** cycle, with only a capacity retention of **13.0%** after **100** cycles. In contrast, the etched 25 and coated metallurgical silicon exhibits a discharge capacity of **3099.1 mAh g⁻¹** in the first cycle, and stables at **791.0 mAh g⁻¹**, with a higher capacity retention of **25.5%**. The results fully demonstrated that ALD Al₂O₃ coating can greatly enhance the cycling stability upon cycling. Moreover, when the etched and coated metallurgical silicon was cycling at high rate of **1C (2 A g⁻¹)**, its 30 discharge capacity stabilizes at **607.5 mAh g⁻¹** after over **1000** cycles, and the Coulombic efficiency stills hold above **99.5%** during the whole cycling, indicating a very impressive cycling stability.

The enhanced electrochemical performance of etched and coated particles could be ascribed to three reasons. Firstly, the nano size of these particles not only shorten the diffusion distance of lithium ions and electrons but also offer higher electrode/electrolyte contact area, benefiting fast kinetic reaction inside the bulk. The enlarged contact area will have negative effect on deteriorating the electrochemical performance if the Si surface is covered with uniform and thin coating layer. Secondly, the nano pores insides the particles can effectively buffer the huge volume changes during the repeated lithiation and delithiation process, thus leading to superior cycling performance with high lithium storage capacity. Lastly, the uniform ALD Al_2O_3 coating layer with only about 3 nm thickness can prevent the direct contact between the electrode and electrolyte with suppressed side reactions and create a stable SEI layer at the electrode/electrolyte interface. In particular, The resulting etched and coated metallurgical silicon particles showed enhanced electrochemical cycling stability and superior lithium storage capacity.

While specific embodiments have been described and illustrated, such embodiments should be considered illustrative only and not as limiting the disclosure as construed in accordance with the accompanying claims.

What is claimed is:

1. A method for producing an anode for a battery comprising:

providing a quantity of metallurgical silicon;

etching the metallurgical silicon; and

depositing a ceramic layer on the etched metal deposited metallurgical silicon.

2. The method of claim **1** further comprising depositing a quantity of a metal on the surface of the quantity of metallurgical silicon to produce a metal deposited metallurgical silicon before etching.

3. The method of claim **2** further comprising reducing the size of the metallurgical silicon into particles having a diameter selected to be between **0.5** and **50** mm.

4. The method of claim **3** wherein the reducing comprises mechanically reducing.

5. The method of claim **4** wherein the mechanical reducing comprises crushing.

6. The method of claim **2** wherein the metal is selected from the group comprising silver, gold, platinum, nickel and iron.

7. The method of claim **6** wherein the metallurgical silicon is immersed in a solution containing a salt of the metal.

8. The method of claim **7** wherein the metal is deposited on to the surface of the metallurgical silicon through a galvanic displacement reaction.

9. The method of claim **1** wherein the ceramic layer comprises a metal oxide.

5 **10.** The method of claim **9** wherein the metal oxide is selected from the group consisting of aluminum oxide, titanium oxide, zirconium oxide and silicon oxide.

10 **11.** The method of claim **1** wherein the ceramic layer comprises a metal oxynitride.

12. The method of claim **11** wherein the metal oxynitride is selected from the group consisting of aluminium oxynitride, titanium oxynitride and tantalum oxynitride.

15 **13.** The method of claim **8** wherein the ceramic layer is selected to have a thickness between **1** and **20** nm.

14. The method of claim **13** wherein the ceramic layer is formed by atomic layer deposition.

20 **15.** An anode for a battery comprising at least one particle of porous metallurgical silicon having a ceramic layer formed thereover.

25 **16.** The anode of claim **15** wherein the particle of porous metallurgical silicon is formed by metal assisted chemical etching a quantity of metallurgical silicon.

17. The anode of claim **16** wherein the ceramic layer is formed by atomic layer deposition.

30 **18.** The anode of claim **17** wherein the ceramic layer is selected to have a thickness of between **1** and **20** nm.

19. The anode of claim **15** wherein a plurality of particles of porous metallurgical silicon are secured in a binder.

20. A lithium ion battery comprising:

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a cathode;

an anode comprising at least one particle of porous metallurgical silicon having a ceramic layer formed thereover; and

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a non-aqueous lithium containing electrolyte between the cathode and anode.