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(54) **NANO-SCALE/NANOSTRUCTURED SI COATING ON VALVE METAL SUBSTRATE FOR LIB ANODES**

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(58) **Field of Classification Search**

None

See application file for complete search history.

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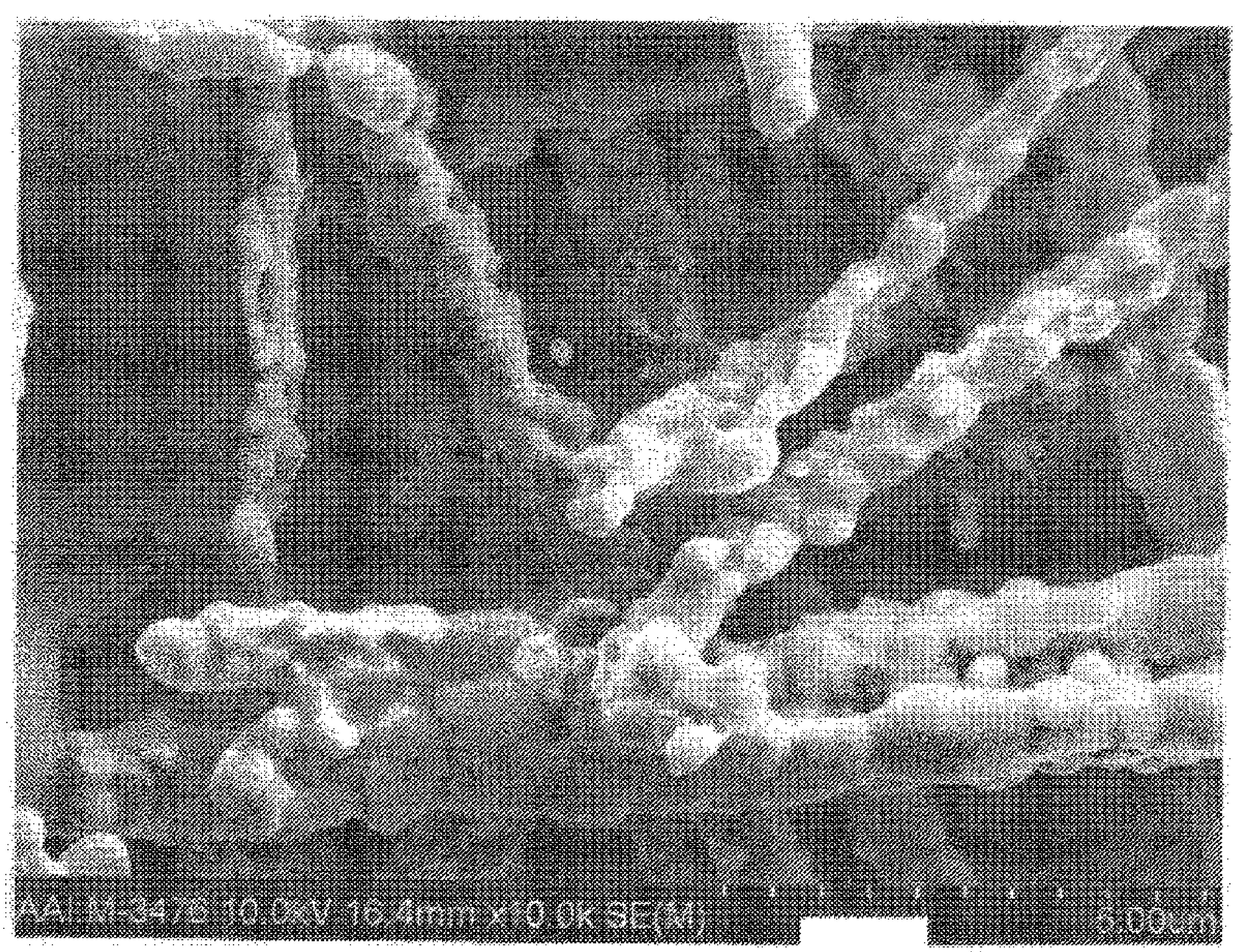
(57) **ABSTRACT**

An improved structure of nano-scaled and nanostructured Si particles is provided for use as anode material for lithium ion batteries. The Si particles are prepared as a composite coated with MgO and metallurgically bonded over a conductive refractory valve metal support structure.

16 Claims, 6 Drawing Sheets



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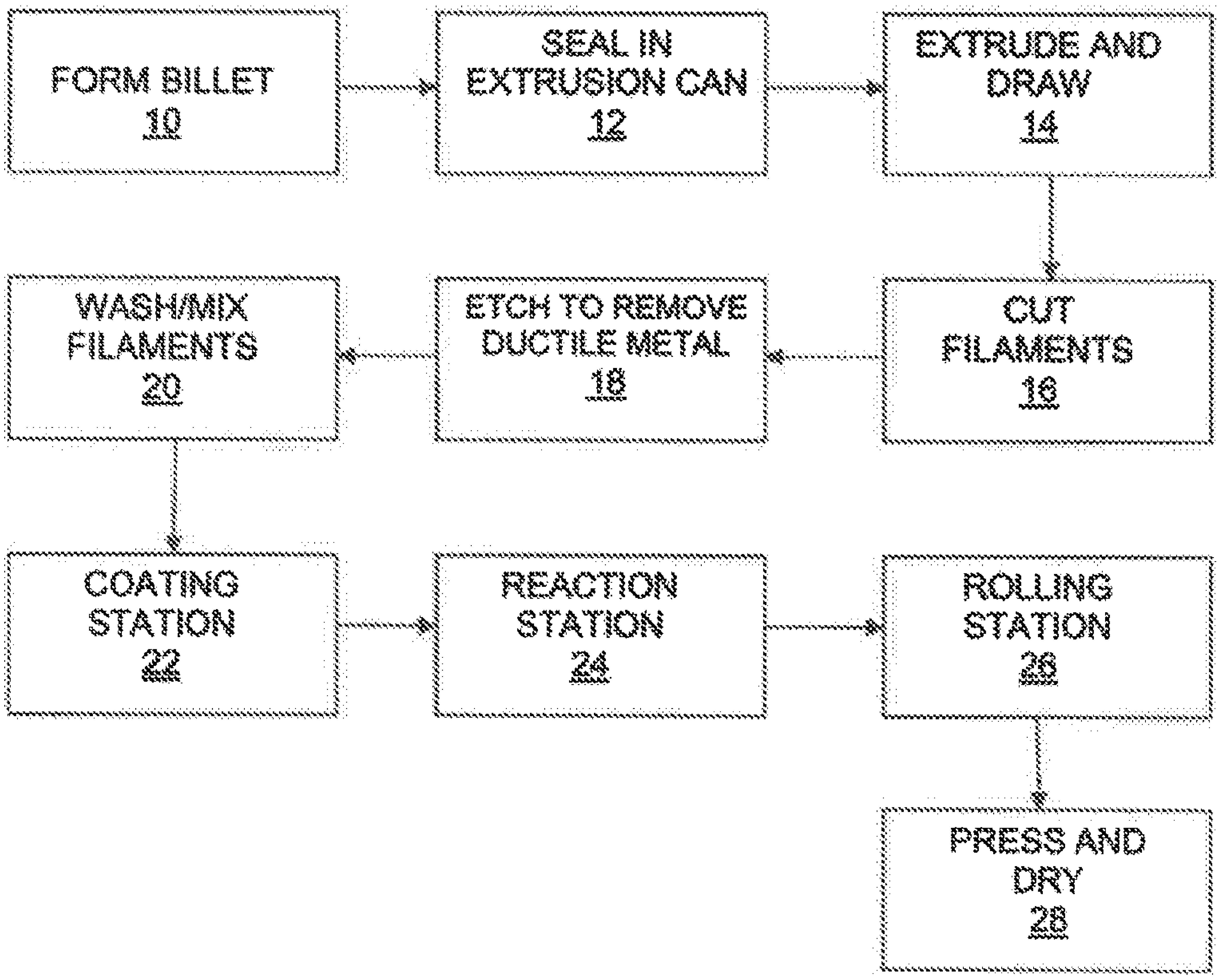
FORM BILLET
10
SEAL IN EXTRUSION CAN
12
EXTRUDE AND DRAW
14
CUT FILAMENTS
16
ETCH TO REMOVE DUCTILE METAL
18
WASH/MIX FILAMENTS
20
COATING STATION
22
REACTION STATION
24
ROLLING STATION
26
PRESS AND DRY
28

FIG. 1

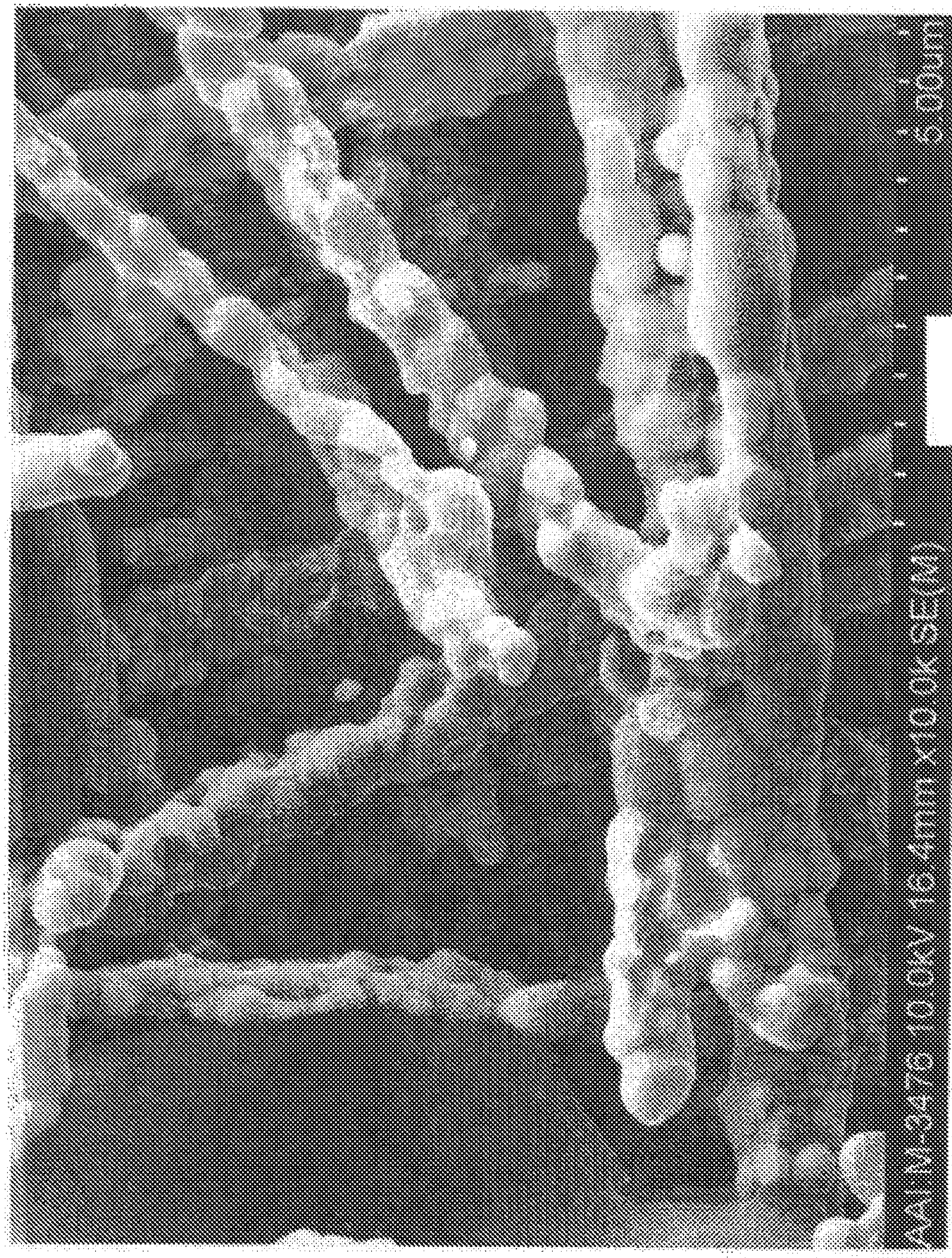

FIG. 2

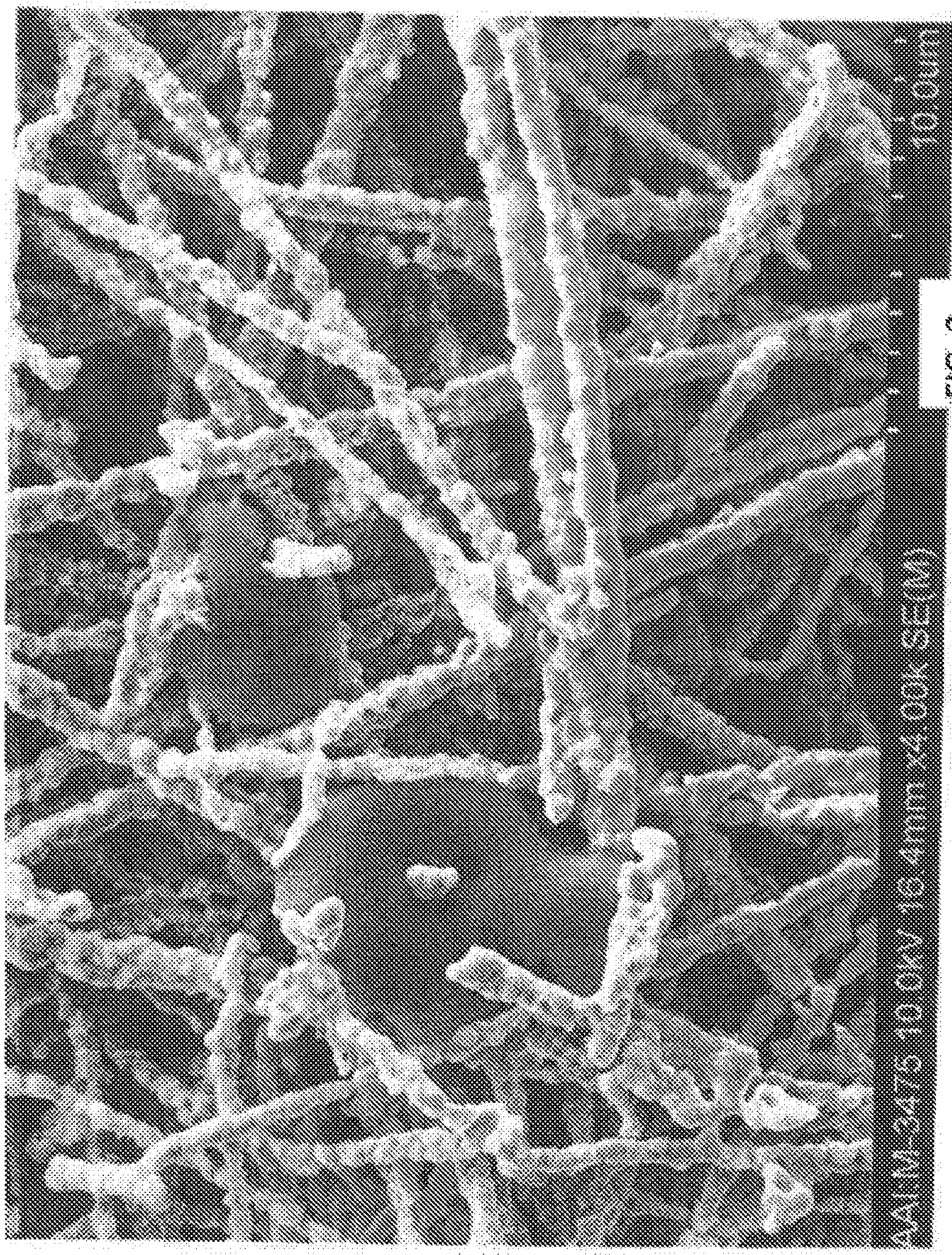

FIG. 3

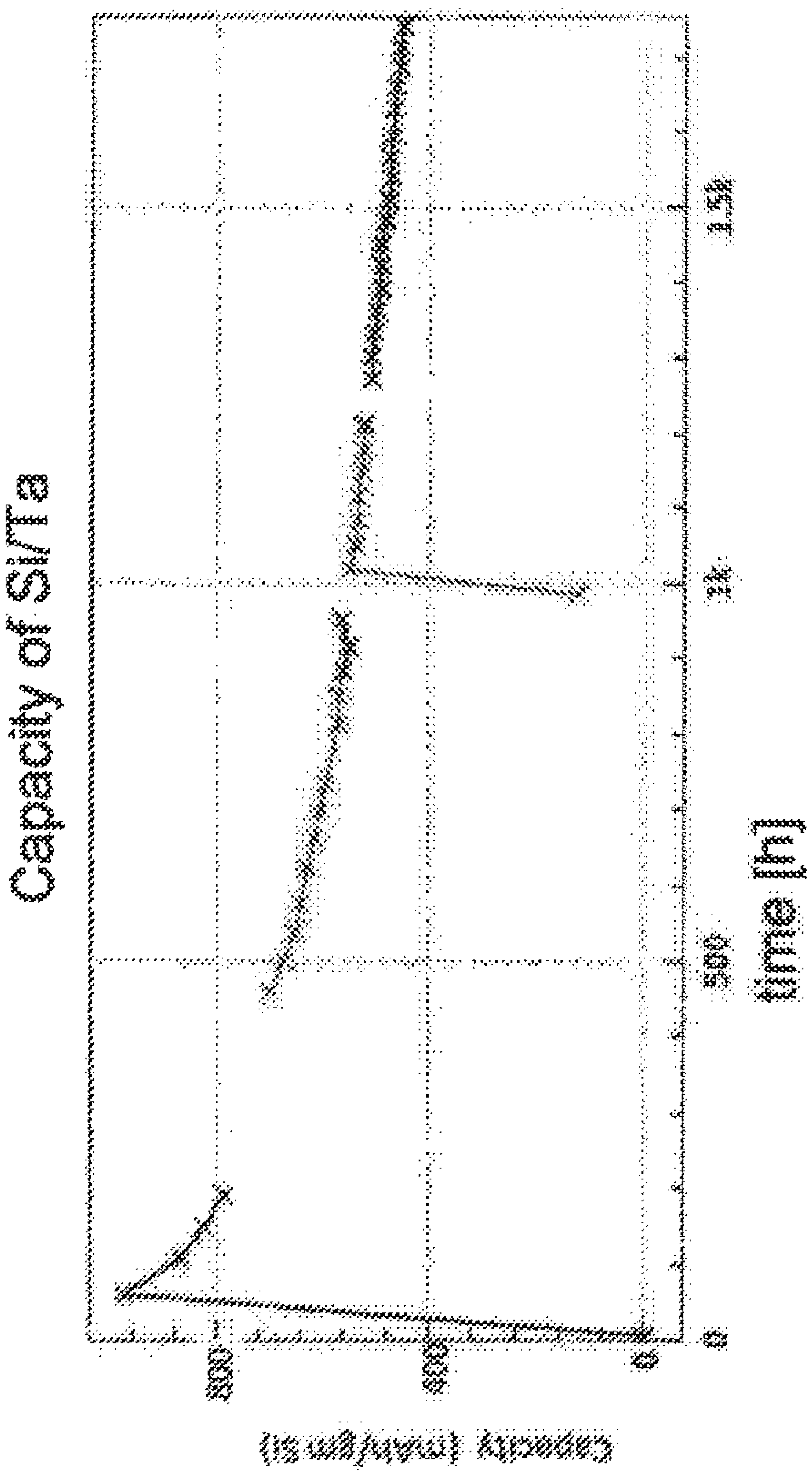
Capacity of Si/Ta
time [h]
Capacity (mAh/gm Si)
0
500
1k
1.5k

FIG. 4

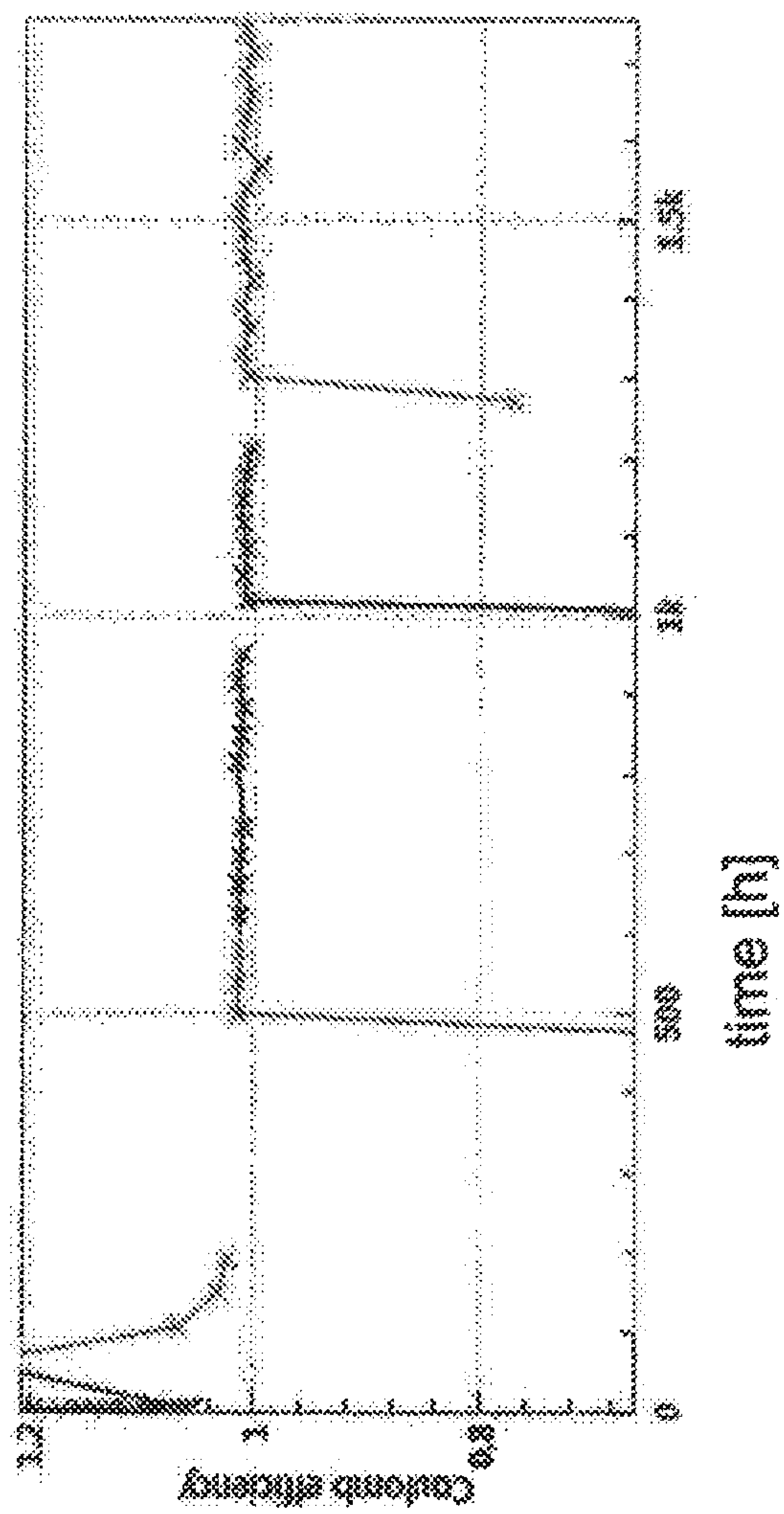
time [h]
Coulomb efficiency
1.2
1
0.8
0
500
1k
1.5k

FIG. 5

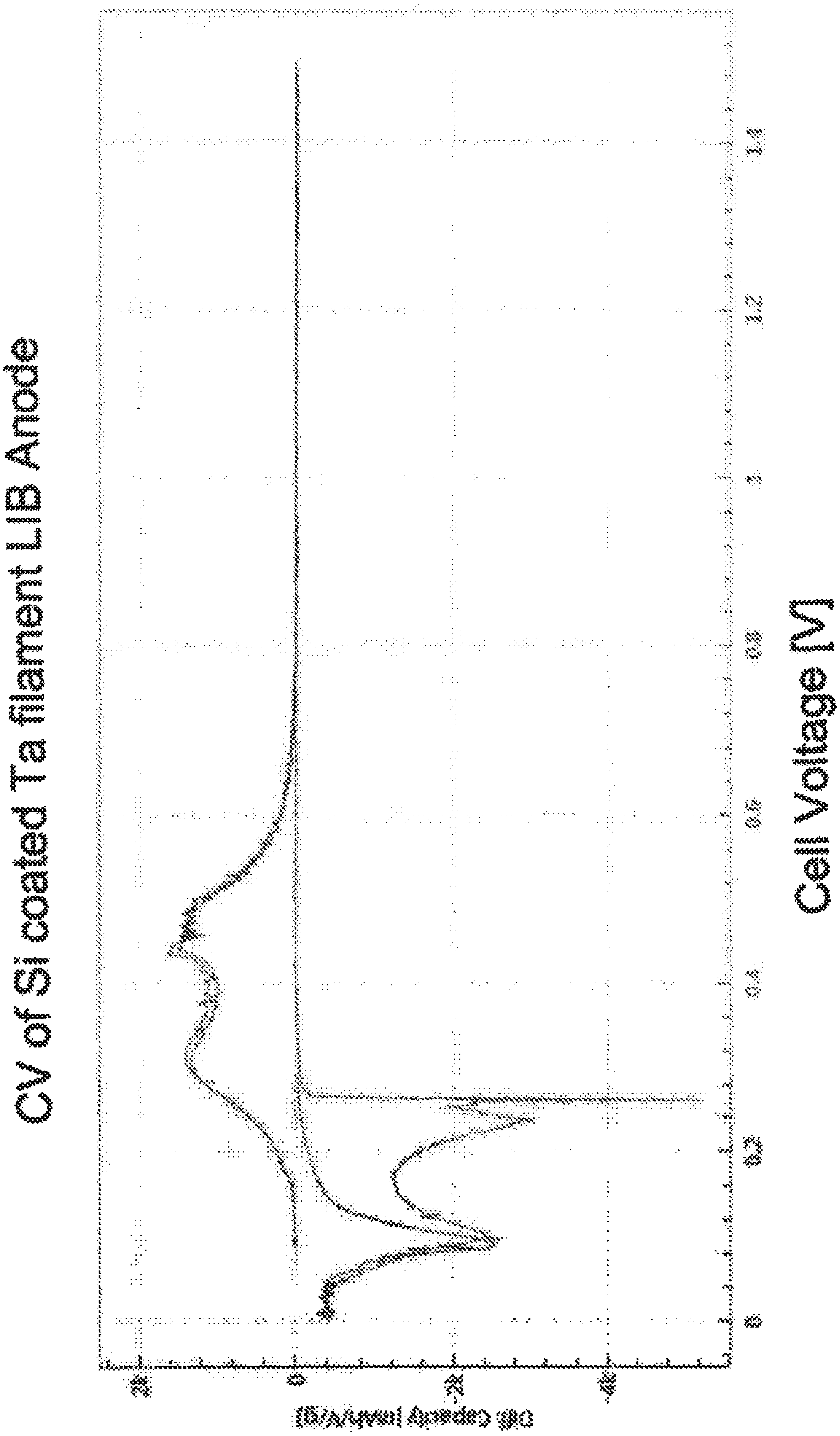
CV of Si coated Ta filament LIB Anode
Cell Voltage [V]
0
0.2
0.4
0.6
0.8
1
1.2
1.4
20
0
-20
-40

FIG. 6

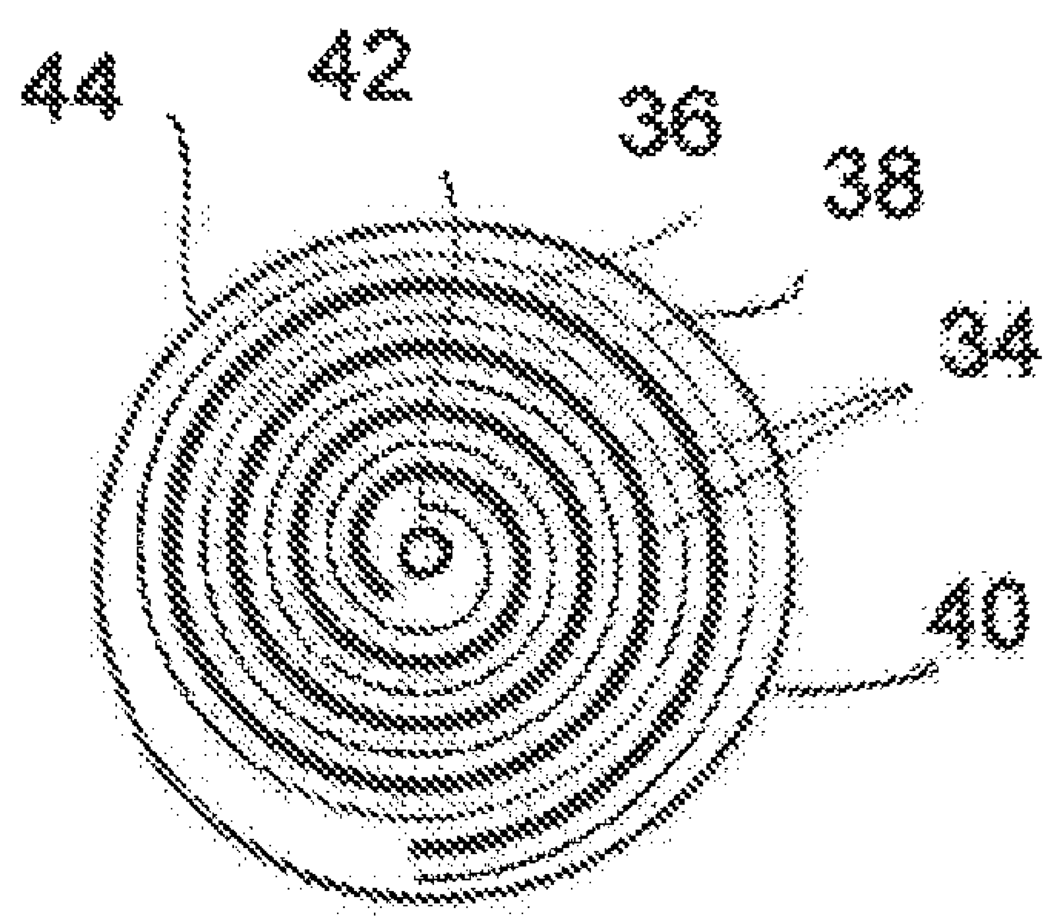

FIG. 7

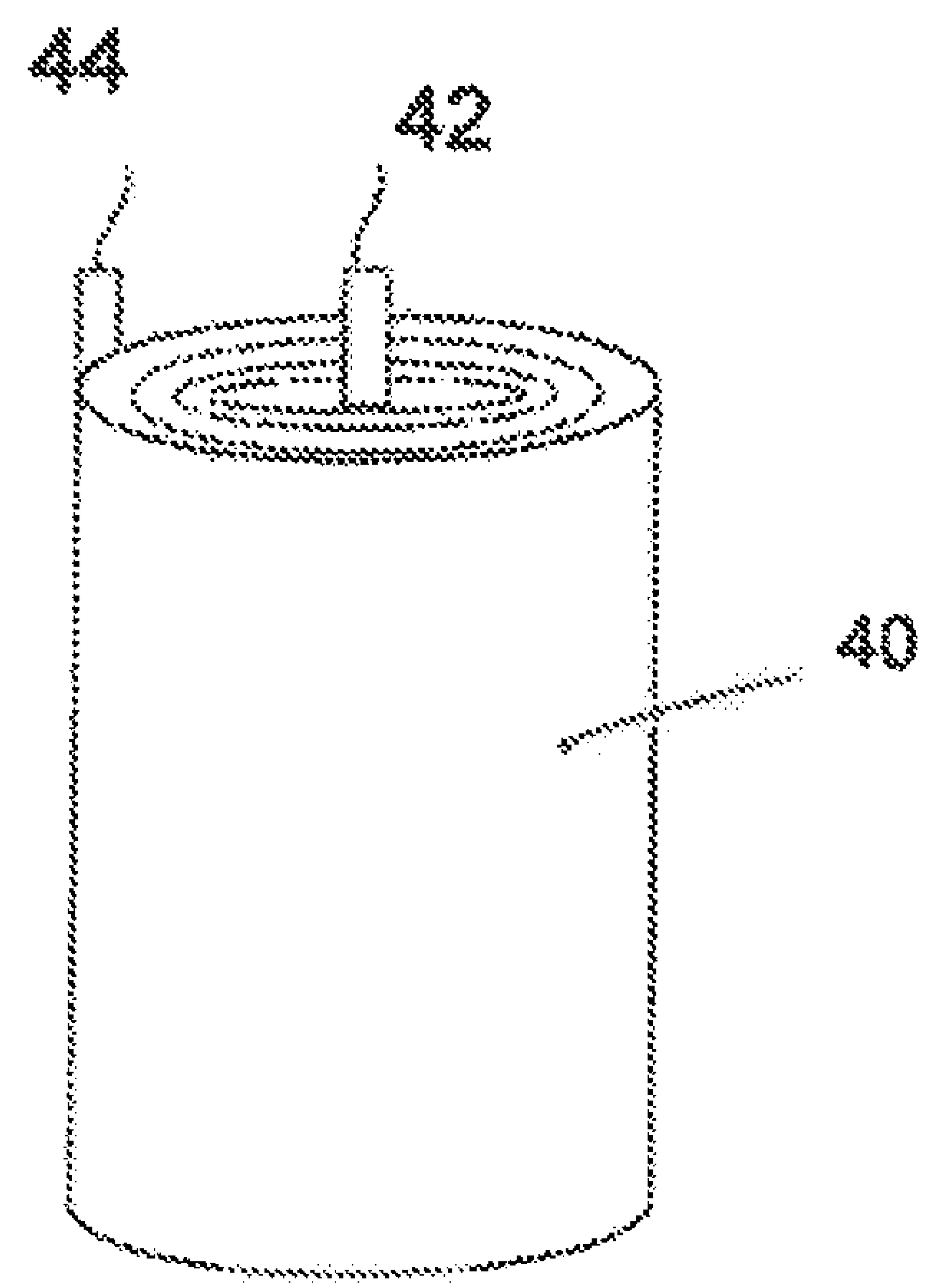

FIG. 8

NANO-SCALE/NANOSTRUCTURED SI COATING ON VALVE METAL SUBSTRATE FOR LIB ANODES

Matter enclosed in heavy brackets [ ] appears in the original patent but forms no part of this reissue specification; matter printed in italics indicates the additions made by reissue; a claim printed with strikethrough indicates that the claim was canceled, disclaimed, or held invalid by a prior post-patent action or proceeding.

CROSS-REFERENCE TO RELATED APPLICATION

This application claims priority from US Provisional Application Ser. No. 62/382,696, filed Sep. 1, 2016, the contents of which are incorporated herein by reference.

FIELD OF INVENTION

The present invention relates to improvements in anode materials for use in lithium ion batteries, and will be described in connection with such utility, although other utilities are contemplated.

BACKGROUND OF THE INVENTION

Silicon is a promising material for high capacity anodes in lithium ion batteries (LIB). When alloyed with lithium, the specific capacity (mAh/g) of silicon is an order of magnitude higher than conventional graphite anode materials. However, silicon exhibits a large volume change (up to 400% expansion and contraction) during lithiation (charging) and delithiation (discharging), respectively. For bulk silicon, this creates structural stress gradients within the silicon and results in fractures and mechanical stress failure (pulverization) thereby decreasing effective electrical contact and lifetime of the silicon anode.

Considerable efforts have been undertaken to overcome this intrinsic issue by controlling the morphology and limiting the size of silicon particles to a size below which silicon is less likely to fracture, approximately 50 nm.

Various attempts to avoid the physical damage caused by silicon's expansion/contraction have included nanoscaled and nanostructured silicon in forms such as thin films; nanowires; nanotubes; nanoparticles; mesoporous materials; and nanocomposites. Most of these approaches do not provide viable, cost effective solutions.

One promising method utilizes Si—MgO composites formed by mechanical alloying/solid phase reaction of SiO_2 and magnesium according to the reaction:

$$2Mg(s)+SiO_2(s)\rightarrow 2MgO(s)+Si(s) \quad \text{(Formula I)}$$

The MgO matrix has shown to buffer the effects of volumetric changes; however, these composites have relatively low electrical conductivity rendering them poorly effective as anode material.

Sub-micron scale, electrochemically active particles dispersed on conductive substrates and supports have long been used for electrochemical cells including fuel cells and batteries. This support structure is an important component with regard to cell efficiency and lifetime. Valve (or refractory) metals particularly, (specifically: Titanium, Niobium, Tantalum, and their alloys) have been used as substrates for electrochemically active materials for over 70 years in application of chemical processing and cathodic protection. These applications utilize the formation of a passivating oxide film over the exposed valve metal areas, as a means of creating a conductive and electrochemically stable support structure for the active material.

Mg has long been used as a magnesiothermic reducing agent for purification of refractory metals. This process is common in production of high capacity, high surface tantalum powders for capacitor applications occurring via the vapor/solid phase reaction:

$$5Mg(g)+Ta_2O_5(s)\rightarrow 5MgO(s)+2Ta(s) \quad \text{(Formula II)}$$

The resulting magnesium oxide forms a surface coating over the host Ta particles, and is removed using mineral acids.

In one aspect the present invention provides electrically active electrode material for use with a lithium ion cell, the electrochemically active material electrode material comprising a valve metal substrate material formed of filaments or particles of a valve metal not larger than about 10 microns in cross section, and coated with metallurgically bonded silicon particles.

In a preferred embodiment, the valve metal is selected from the group consisting of tantalum, niobium, an alloy of tantalum, an alloy of niobium, hafnium, titanium and aluminum.

In another preferred embodiment, the valve metal filaments have a thickness of less than about 5-10 microns, and preferably have a thickness below about 1 micron.

In one aspect the silicon coating is comprised of nanoscaled nanoparticles.

In another aspect the silicon particles are coated on the valve metal substrate in a stabilizing MgO matrix.

In still another aspect, electrically active electrode material as above described is formed into an anode.

The present invention also provides a method of forming an electrode substrate useful for forming a lithium ion battery comprising the steps of: (a) providing valve metal substrate material formed of filaments or particles of a valve metal not larger than about 10 microns in cross section; and, (b) coating the valve metal substrate material with metallurgically bonded silicon formed by a magnesiothermic reaction of magnesium with silica and the valve metal.

In one aspect of the method, the magnesiothermic reaction is conducted under vacuum or in an inert gas at elevated temperature, preferably an elevated temperature selected from a group consisting of 800-1200° C., 900-1100° C. and 950-1050° C.

In another aspect of the method, the magnesiothermic reaction is conducted for time selected from 2-10 hours, 4-8 hours and 5-6 hours.

In yet another aspect of the method includes the step of removing at least some of the magnesium oxide following the reaction by acid etching.

In one preferred aspect of the method, the valve metal is selected from the group consisting of tantalum, niobium, an alloy of tantalum, an alloy of niobium, hafnium, titanium and aluminum.

In another preferred aspect of the method, the filaments or fibers have a thickness of less than about 5-10 microns, and preferably a thickness below about 1 micron.

In another aspect of the method, the electrochemically active material comprises silicon nanoparticles.

The present invention also provides a lithium ion battery comprising a case containing an anode and a cathode separated from one another, and an electrolyte, wherein the anode is formed of electrically active electrode material comprising the steps of: (a) providing valve metal substrate material formed of filaments or particles of a valve metal not larger than about 10 microns in cross section; and, (b) coating the valve metal substrate material with metallurgically bonded silicon formed by a magnesiothermic reaction of magnesium with silicon and the valve metal.

In yet another aspect of the cell, the valve metal is selected from the group consisting of tantalum, niobium, an alloy of tantalum, an alloy of niobium, hafnium, titanium and aluminum.

SUMMARY OF THE INVENTION

The present invention provides a combination reaction (or co-reaction) of Mg de-oxidation of a refractory metal substrate and substantially simultaneous reduction of SiO_2 (silica) to produce nanoscale coating of nanostructured Si inside a stabilizing MgO coating, both of which are metallurgically bonded to a valve metal substrate. The oxide impurities in the valve metal and the SiO_2 react substantially concurrently to form a nanoscale nanostructure of pure Si which is firmly bonded to the valve metal substrate, e.g. tantalum (Ta) via the reaction:

$$9Mg(g)+2Ta_2O_5(s)+2SiO_2 \rightarrow 4Ta(s)+2Si(s)+9MgO(s) \quad \text{(Formula III)}$$

The overall process involves mixing valve metal particles, e.g., tantalum, with SiO_2 nanoparticles of 4 to 200 micron size, preferably 10 to 100 micron size, more preferably 20 to 50 micron size in an aqueous based solution or gel. In one method, SiO_2 particles are impregnated into a preformed, porous mat of tantalum fibers as an aqueous gel of SiO_2 nanoparticles. In another method, loose particles of tantalum are mixed with SiO_2 particles. The resulting mixture is then subjected to a magnesiothermic reduction via Formula III under vacuum or inert gas at temperatures between 900-1100° C. for 2 to 10 hrs. The magnesium reduces the silica and the oxide impurities within the tantalum fiber thereby permitting the silicon to metallurgically bond to the tantalum substrate. The magnesium oxide which results may remain, or be removed for example, by acid etching. The resulting structure is a spongy, high surface area conductive, electrochemically stable refractory metal substrate coated with a composite of sub-micron Si particles within a MgO coating.

BRIEF DESCRIPTION OF THE DRAWINGS

Further features and advantages of the present invention will be seen from the following detailed description, taken in conjunction with the accompanying drawings, wherein:

FIG. **1** is a schematic block diagram of a process for providing anode material in accordance with the present invention;

FIGS. **2** and **3** are SEM photographs at two different magnifications showing nanoscaled nanostructure of Si particles metallurgically bonded to Ta support particles in accordance with the present invention;

FIG. **4** plots capacity versus time of anode material made in accordance with the present invention;

FIG. **5** plots coulomb efficiency versus time of anode material made in accordance with the present invention;

FIG. **6** plots differential capacity versus cell voltage for a lithium ion battery anode made in accordance with the present invention;

FIG. **7** is a cross-sectional view of a rechargeable battery in accordance with the present invention; and

FIG. **8** is a perspective view of a battery made in accordance with the present invention.

DETAILED DESCRIPTION OF THE INVENTION

In one embodiment of the invention, the refractory metal is formed of micron size (e.g. not larger than about 10 microns in across) tantalum filaments formed as described for example, in my earlier U.S. Pat. Nos. 9,155,605, 5,869,196, 7,146,709, and PCT WO2016/187143 A1, the contents of which are incorporated herein by reference.

Referring to FIG. **1**, the production process starts with the fabrication of valve metal filaments, preferably tantalum, by combining filaments or wires of tantalum with a ductile material, such as copper to form a billet at step **10**. The billet is then sealed in an extrusion can in step **12**, and extruded and drawn in step **14** following the teachings of my '196 U.S. patent. The extruded and drawn filaments are then cut or chopped into short segments, typically 1/16th-1/4th inch long at a chopping station **16**. Preferably the cut filaments all have approximately the same length. Actually, the more uniform the filament, the better. The chopped filaments are then passed to an etching station **18** where the ductile metal is leached away using a suitable acid. For example, where copper is the ductile metal, the etchant may comprise nitric acid.

Etching in acid removes the copper from between the tantalum filaments.

After etching, one is left with a plurality of short filaments of tantalum. The tantalum filaments are then washed in water in a washing station **20**, and the wash water is partially decanted to leave a slurry of tantalum filaments in water. The slurry of tantalum particles in water is then mixed with fine, e.g. 4 to 200 micron size silica particles in water, in a coating station **22**, forming a spongy mass. The coated spongy mass is then dried and subjected to magnesiothermic reaction by treating under vacuum or in an inert gas at 800 to 1200° C., preferably 900 to 1100° C., more preferably 950 to 1050° C., for 2 to 10 hours, preferably 4 to 8 hours, more preferably 5 to 6 hours at a reaction station **24**. The magnesium reduces the silica and the oxide impurities within the tantalum fibers simultaneously permitting silicon to metallurgically bond to the tantalum fibers. Any magnesium oxide which results may remain, but preferably is removed for example by acid etching. On the other hand, it is not necessary to completely remove any copper which may be left over from the extrusion and drawings steps, since the copper also would metallurgically bond to the silicon. The resulting structure is a spongy, high surface area, conductive electrochemically stable tantalum metal substrate mass coated with a composite of sub-micron Si particles coated with a MgO matrix. The resulting spongy mass may then be mixed with water, and cast as a mat at a rolling station **26**. The resulting mat is then further compressed and dried at a drying station **28**.

As an alternative to coating and rolling a thin sheet may be formed by spray casting the slurry onto to a substrate, excess water removed and the resulting mat pressed and dried as before.

There results a highly porous thin sheet of Si/MgO composite or Si coated tantalum filaments substantially uniform in thickness.

As reported in my aforesaid PCT application, an aqueous slurry of chopped filaments will adhere together sufficiently so that the fibers may be cast as a sheet which can be pressed and dried into a stable mat. This is surprising in that the metal filaments themselves do not absorb water. Notwithstanding, as long as the filaments are not substantially thicker than about 10 microns, they will adhere together. On the other hand, if the filaments are much larger than about 10 microns, they will not form a stable mat or sheet. Thus, it is preferred that the filaments have a thickness of less than about 10 microns, and preferably below 1 micron thick. To ensure an even distribution of the filaments, and thus ensure production of a uniform mat. the slurry preferably is subjected to vigorous mixing by mechanical stirring or vibration.

The density or porosity of the resulting tantalum mat may be varied simply by changing the final thickness of the mat.

Also, if desired, multiple layers may be stacked to form thicker mats that may be desired, for example, for high density applications.

The resulting tantalum mat comprises a porous mat of sub-micron size Si or Si/MgO composite coated tantalum filaments in contact with one another, forming a conductive mat.

Alternatively, in a preferred embodiment of the invention, the raw tantalum filaments may be formed as mats of electrode material by casting and rolling above described are then coated with silicon nanoparticles by magnesiothermic reduction as above described, e.g., by dipping the tantalum mat into an aqueous based solution containing fine silica in water, and then heating under vacuum or inert gas as above described.

The Si/Ta structure as shown in FIGS. **2** and **3** is that of valve metal structure that is coated with a layer of nanoscaled nanostructure Si particles. The MgO can act as a stabilizing buffer against the degradation of the Si during cycling as the LIB anode. Although it is preferred that the MgO matrix is removed, using mineral acids, to reveal a nanoscaled nanostructure of the Si particles which are metallurgically bonded to the Ta support particles.

The resulting materials are tested for capacity over time, coulomb efficiency over time and differential capacity over cell voltage, and the results shown in FIGS. **4**-**6**.

The resulting Si coated refractory material can be formed into useful LIB anodes via any standard manufacturing method, including, but not limited to: thin wet-lay methods deposited on a current collector, with or without conductive carbon additive; calendared fabrics; coins; etc. For example, referring to FIGS. **7** and **8**, the coated mats are then assembled in a stack between separator sheets **36** to form positive (anode) and negative (cathode) electrodes **38**, **40**. The electrodes **38**, **40** and separator sheets **36** are wound together in a jelly roll and inserted in the case **42** with a positive tab **44** and a negative tab **46** extending from the jelly roll in an assembly station **48**. The tabs can then be welded to exposed portions of the electrode substrates, and the case filled with electrolyte and the case sealed. The result is a high capacity rechargeable battery in which the electrode material comprises extremely ductile fine metal composite filaments capable of repeated charging and draining without adverse effects. Other methods are also contemplated.

Various changes may be made in the above invention without departing from the spirit and scope thereof. For example, the invention has been described particularly in connection with silicon, other materials such as germanium advantageously may be employed. Still other changes may be made without departing from the spirit and scope of the invention.

The invention claimed is:

1. An electrically active electrode material for use with a lithium ion cell, the electrochemically active electrode material comprising a substrate material consisting of individual filaments of a valve metal selected from the group consisting of tantalum, niobium, an alloy of tantalum, an alloy of niobium**[**,**]** *and an alloy of* hafnium, **[**titanium and aluminum,**]** not larger than about 10 microns across, which filaments are adhered together to form a mat or porous sheet and wherein the individual filaments of the mat or porous sheet are coated with a coating of crystalline silicon **[**inside**]** *in* a stabilizing magnesium oxide **[**coating**]** *matrix*, wherein the silicon is metallurgically bonded to the valve metal filaments.

2. The electrically active electrode material of claim **1**, wherein the valve metal filaments have a thickness of less than 10 microns.

3. The electrically active electrode material of claim **1**, wherein the valve metal filaments have a thickness below about 1 micron.

4. The electrically active electrode material of claim **1**, formed into an anode.

5. A method of forming an electrode substrate useful for forming a lithium ion battery comprising the steps of:

(a) providing valve metal substrate material formed of individual filaments of a valve metal selected from the group consisting of tantalum, niobium, an alloy of tantalum, an alloy of niobium**[**,**]** *and an alloy of* hafnium, **[**titanium and aluminum,**]** not larger than about 10 microns across;

(b) forming the individual filaments of step (a) into a mat or porous sheet; and

(c) subjecting the mat or porous sheet of step (b) and silica to a simultaneous magnesiothermic co-reaction with magnesium to produce a coating of crystalline silicon **[**inside**]** *in* a stabilizing magnesium oxide **[**coating**]** *matrix*, wherein the silicon coating is metallurgically bonded to the individual valve metal filaments.

6. The method of claim **5**, wherein the magnesiothermic co-reaction is conducted under vacuum or in an inert gas at elevated temperature of 800-1200° C.

7. The method of claim **6**, wherein the elevated temperature is 900-1100° C.

8. The method of claim **6**, wherein the magnesiothermic co-reaction is conducted for 2-10 hours.

9. The method of claim **5**, wherein the filaments have at thickness of less than 10 microns.

10. The method of claim **5**, wherein the filaments have a thickness below about 1 micron.

11. A lithium ion battery comprising a case containing an anode and a cathode separated from one another, and an electrolyte, wherein the anode is formed of electrically active electrode material as claimed in claim **1**.

12. The method of claim **6**, wherein the elevated temperature is 950-1050° C.

13. The method of claim **6**, wherein the magnesiothermic co-reaction is conducted for 4-8 hours.

14. The method of claim **6**, wherein the magnesiotheimic co-reaction is conducted for 5-6 hours.

15. The electrically active electrode material of claim **1**, wherein the valve metal filaments have a thickness of less than 5 microns.

16. The method of claim **5**, wherein the filaments have a thickness of less than 5 microns.

* * * * *