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

(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.

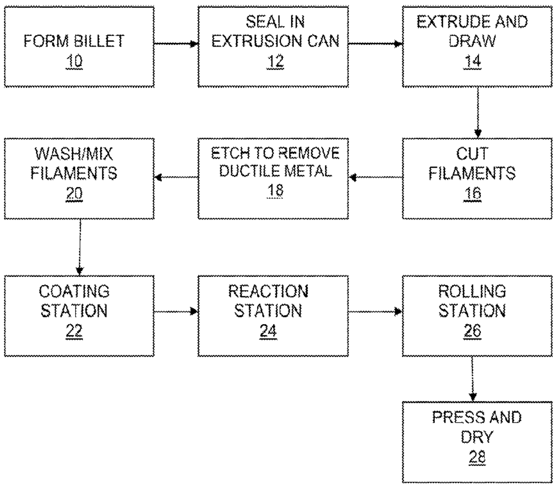

FIG. 1

WO 2018/045339 A1

[Continued on next page]

Published:

— *with international search report (Art. 21(3))*

Nano-scale/Nanostructured Si coating on Valve Metal Substrate for LIB Anodes

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.

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 50nm.

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:

$$2Mg\ (s) + SiO_2\ (s) \rightarrow 2MgO\ (s) + Si\ (s)$$

(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:

$$5Mg\ (g) + Ta_2O_5\ (s) \rightarrow 5MgO\ (s) + 2Ta\ (s)$$

(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.

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:

$$9Mg\ (g) + 2Ta_2O_5\ (s) + 2SiO_2 \rightarrow 4Ta\ (s) + 2Si\ (s) + 9MgO\ (s)$$

(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.

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.

In one, one embodiment of the invention, the refractory metal is formed of micron size (e.g. not larger than about 10 microns in cross section) tantalum particles formed as described for example, in my earlier US Pat. No. 9,155,601, US Pat No. 5,869,196, US Pat. No. 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 drawing 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 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.
2. The electrically active electrode material of claim 1, wherein the valve metal is selected from the group consisting of tantalum, niobium, an alloy of tantalum, an alloy of niobium, hafnium, titanium and aluminum.
3. The electrically active electrode material of claim 1, or claim 2, wherein the valve metal filaments have a thickness of less than about 5-10 microns, preferably a thickness below about 1 micron.
4. The electrically active electrode material of any one of claims 1-3, wherein the silicon coating is comprised of nanoscaled nanoparticles.
5. The electrically active electrode material of any one of claims 1-4, wherein the silicon particles are coated on the valve metal substrate in a stabilizing MgO matrix.
6. The electrically active electrode material of any one of claims 1-5, formed into an anode.
7. 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.
8. The method of claim 7, wherein the magnesiothermic reaction is conducted under vacuum or in an inert gas at elevated temperature.
9. The method of claim 8, wherein the elevated temperature is selected from a group consisting of 800-1200°C, 900-1100°C and 950-1050°C, and/or wherein

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

10. The method of any one of claims 7-9, and including the step of removing at least some of the magnesium oxide following the reaction by acid etching.
11. The method of any one of claims 7-10, wherein the valve metal is selected from the group consisting of tantalum, niobium, an alloy of tantalum, an alloy of niobium, hafnium, titanium and aluminum.
12. The method of any one of claims 7-11, wherein the filaments or fibers have at thickness of less than about 5-10 microns, preferably a thickness below about 1 micron.
13. The method of any one of claims 7-12, wherein the electrochemically active material comprises silicon nanoparticles.
14. 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 any one of claims 1-5.
15. The cell of claim 14, wherein the valve metal is selected from the group consisting of tantalum, niobium, an alloy of tantalum, an alloy of niobium, hafnium, titanium and aluminum.

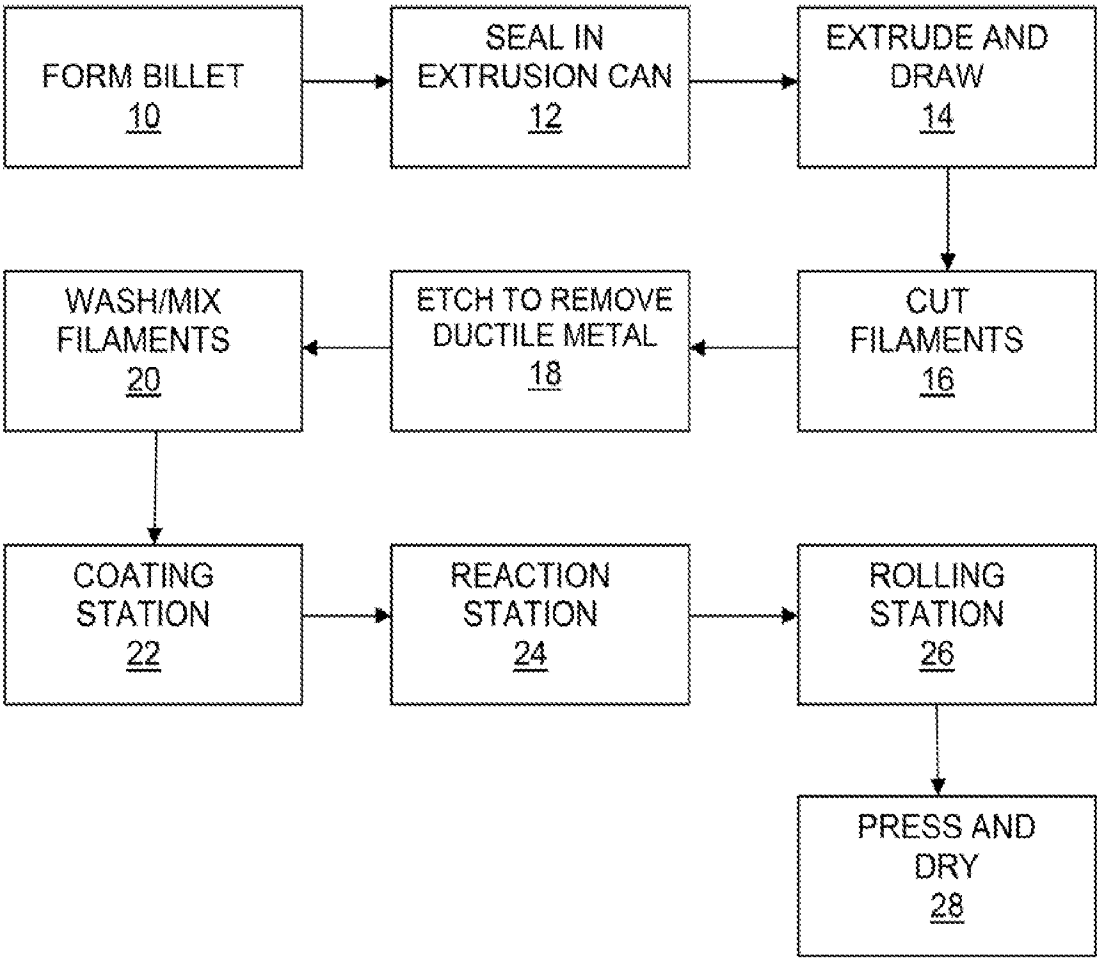
FORM BILLET
10
SEAL IN EXTRUSION CAN
12
EXTRUDE AND DRAW
14
CUT FILAMENTS
16
ETCH TO REMOVE DUCTILE METAL
18
WASH/MIX FILAMENTS
20
COATING STATION
22
REACTION STATION
24
ROLLING STATION
26
PRESS AND DRY
28

FIG. 1

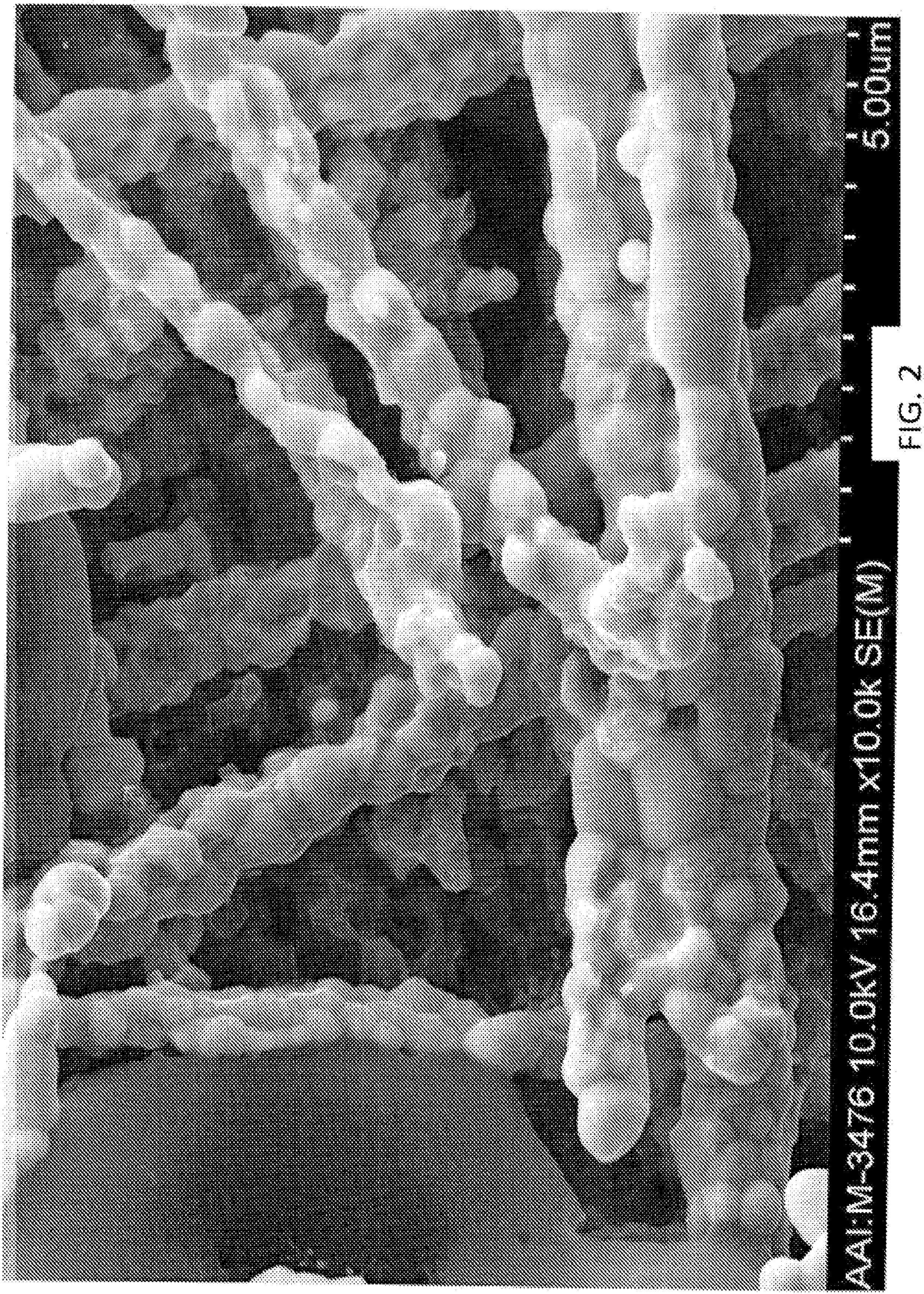

FIG. 2

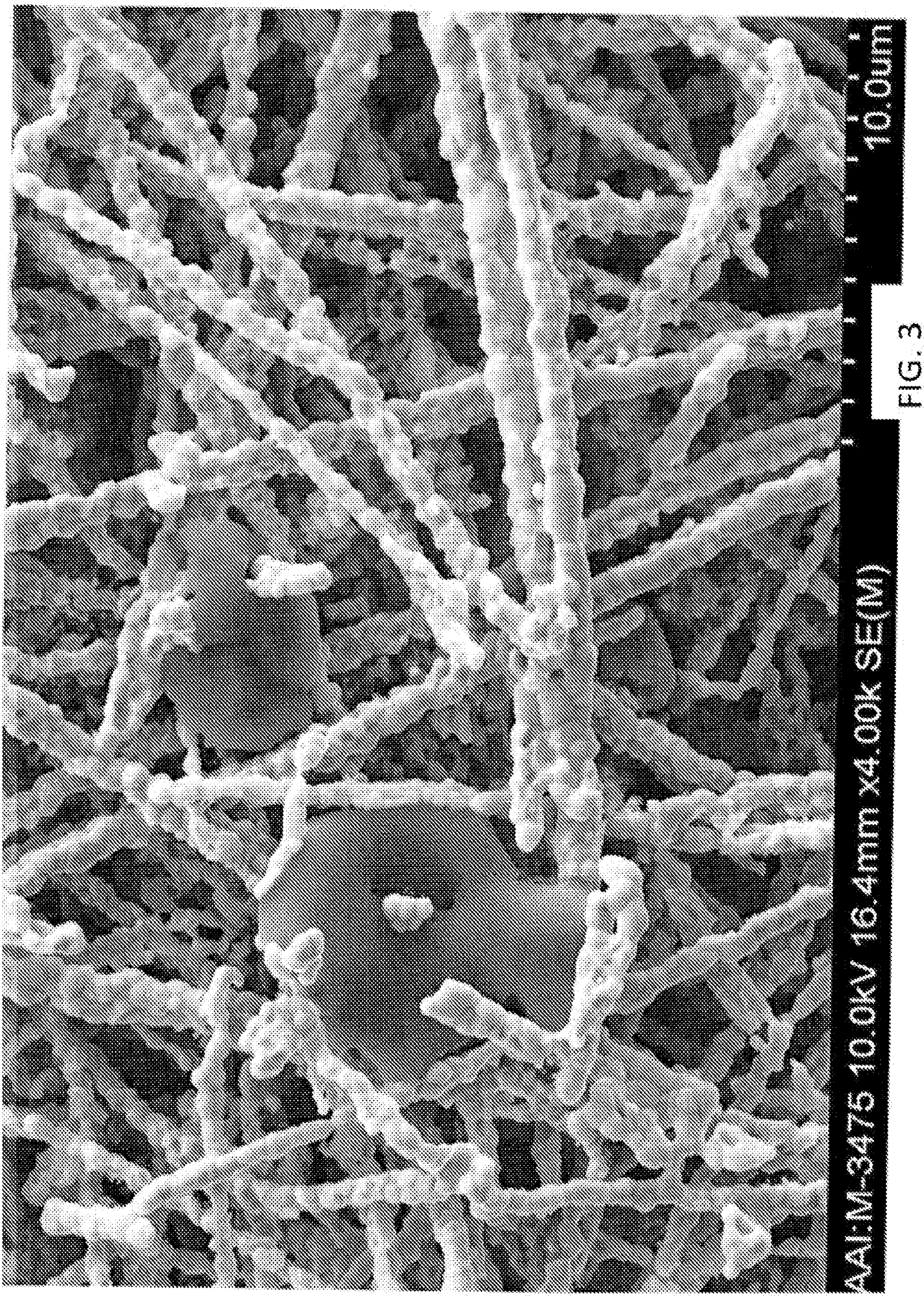

FIG. 3

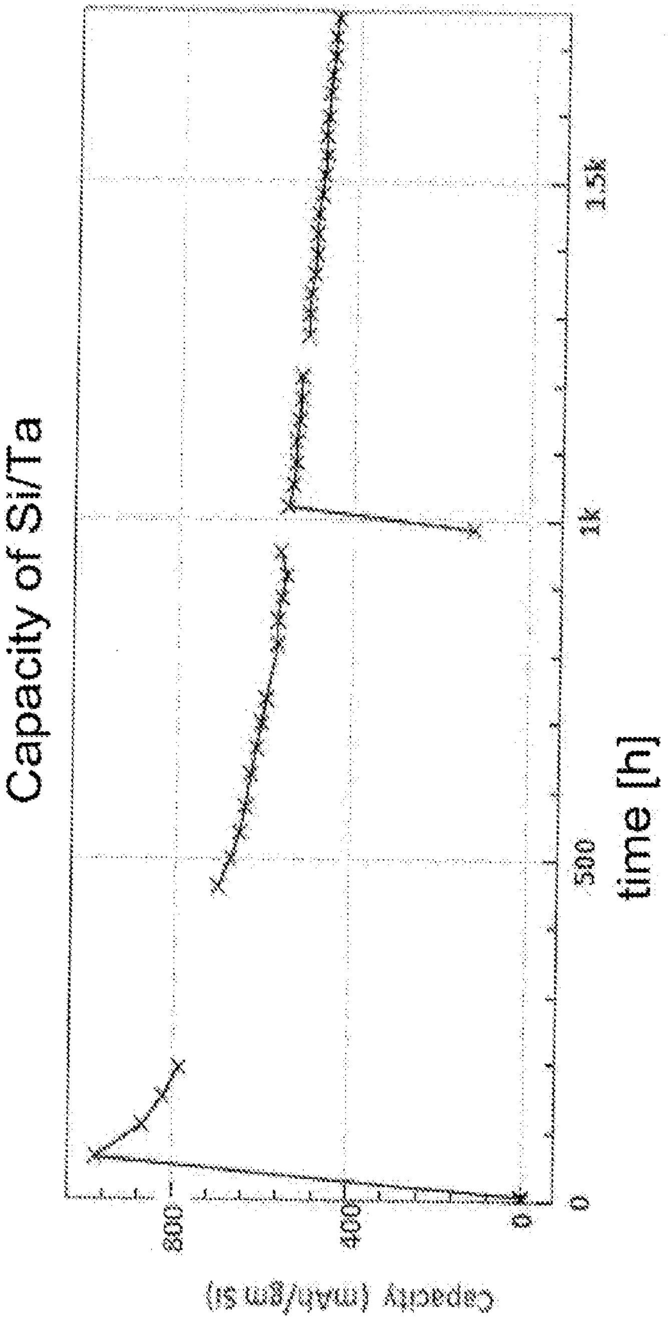
Capacity of Si/Ta
Capacity (mAh/gm Si)
800
400
0
0
500
1k
1.5k
time [h]

FIG. 4

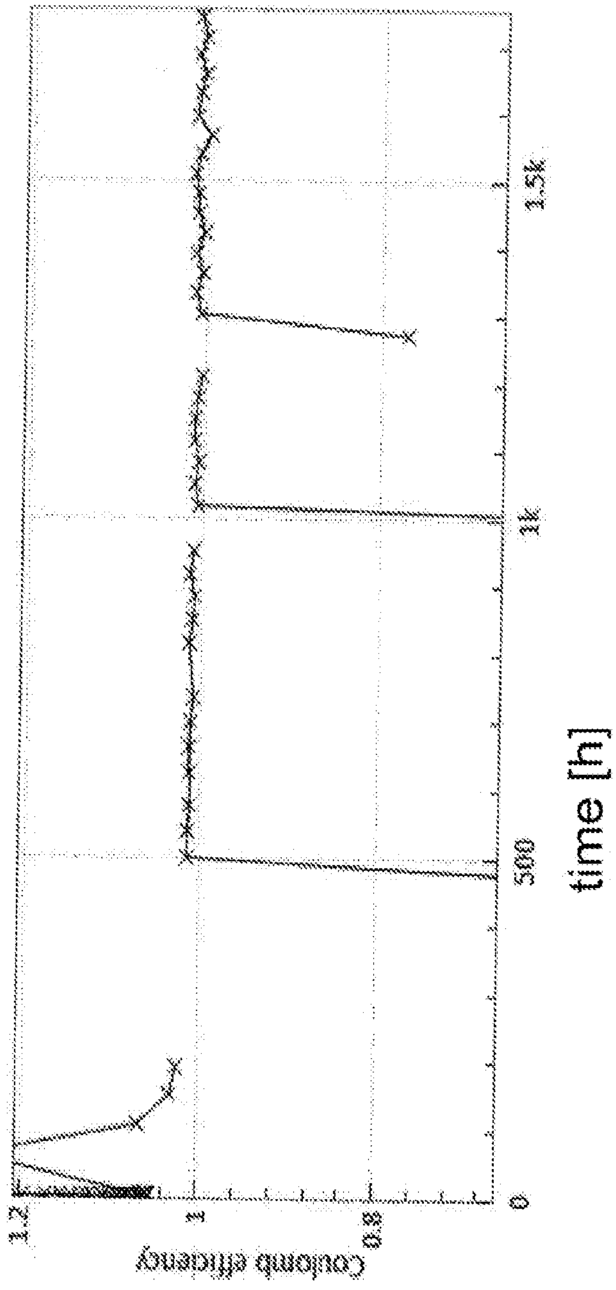
Coulomb efficiency
1.2
1
0.8
0
500
1k
1.5k
time [h]

FIG. 5

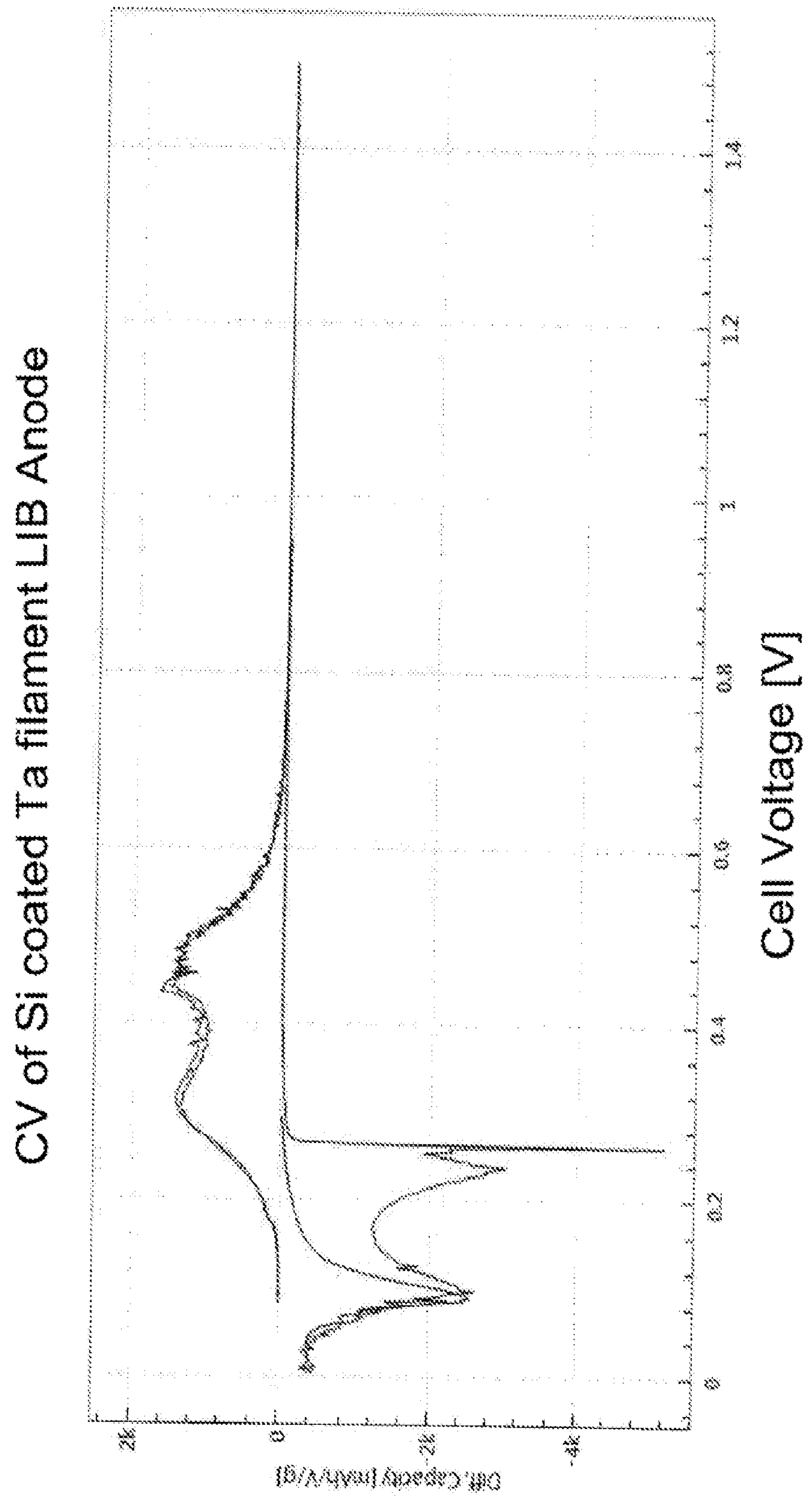
CV of Si coated Ta filament LIB Anode
2k
0
-2k
-4k
Diff. Capacity [mAh/V/g]
0
0.2
0.4
0.6
0.8
1
1.2
1.4
Cell Voltage [V]

FIG. 6

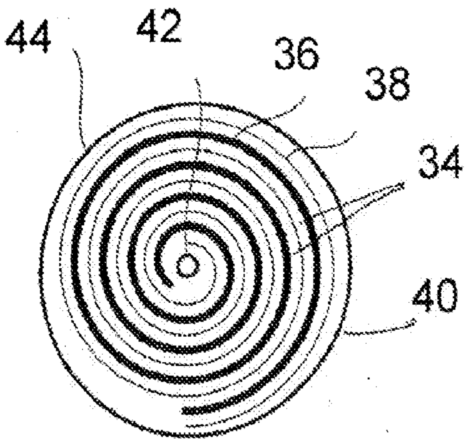

FIG. 7

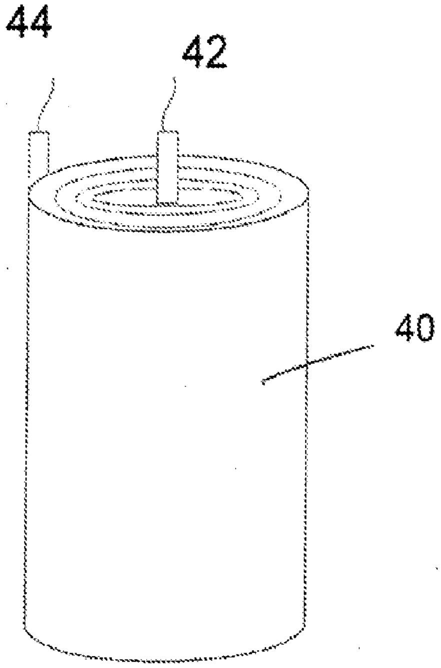

FIG. 8

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 17/49950

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - C01B 33/023, C23C 20/06, H01M 4/36, H01M 4/134, H01M 4/74, H01M 4/13 (2-017.01)
CPC - H01M 4/74, H01M 4/661, H01M 4/386, H01M 4/1395, H01M 4/0404, H01M 10/0525, H01M 4/134

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
See Search History Document

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
See Search History Document

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
See Search History Document

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X -- Y	US 2011/0189510 A1 (CARACCIOLO et al), 04 August 2011 (04.08.2011), figure 8, para [0016], [0022]-[0025], [0036]-[0037], [0040].	1-3 ---- 7-10
Y	US 2015/0028263 A1 (WANG et al), 29 January 2015 (29.01.2015), para [0009], [0030]-[0031], [0035], [0047], [0050], [0054]-[0056], [0060].	7-10
A	US 8435676 B2 (ZHAMU et al, 07 May 2013 (07.05.2013), entire document.	1-3, 7-10
A	US 2012/0094192 A1 (QU et al), 19 April 2012 (19.04.2012), entire document.	1-3, 7-10
X,P	WO 2016/187143 A1 (COMPOSITE MATERIALS TECHNOLOGY INC), 24 November 2016 (24.11.2016), entire document.	1-3

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search 25 October 2017	Date of mailing of the international search report 16 NOV 2017
Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-8300	Authorized officer: Lee W. Young PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 17/49950

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☒ Claims Nos.: 4-6, 11-15
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.