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(54) **TITANIUM DIBORIDE NANOTUBES FOR TRAPPING GASES IN LITHIUM ION BATTERIES**

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(57) **ABSTRACT**

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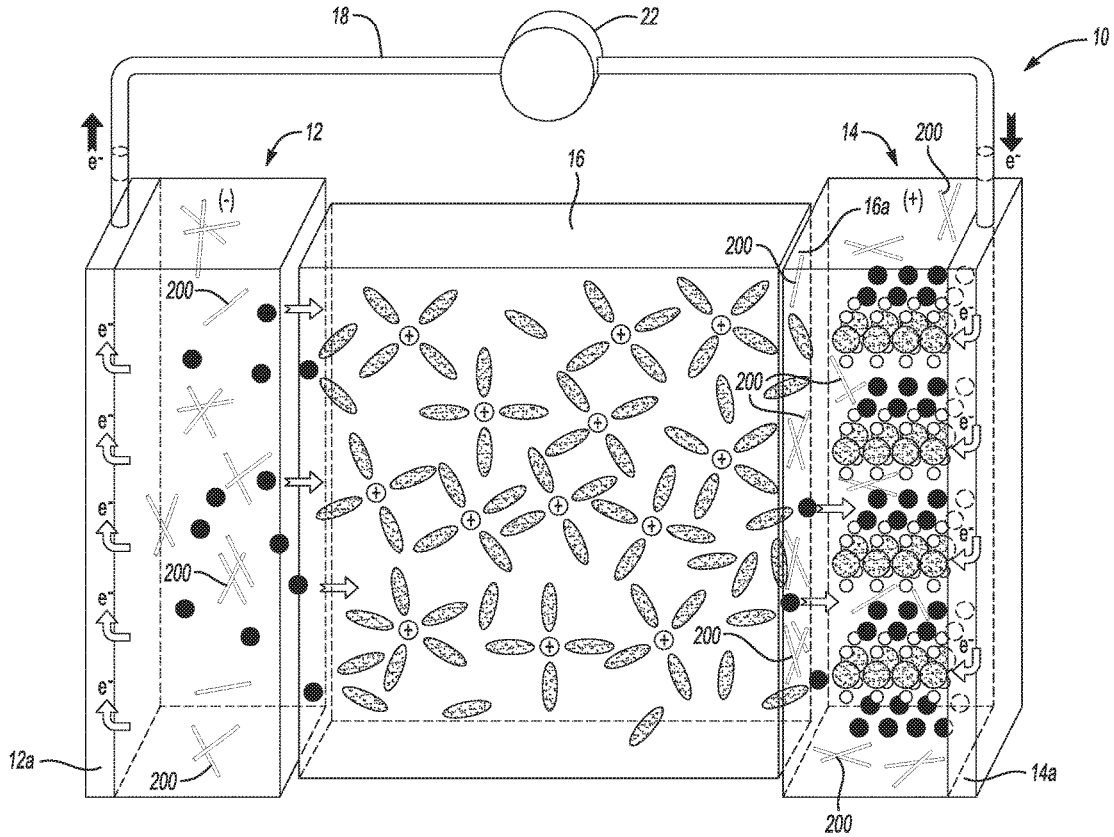
A lithium ion battery includes an electrolyte maintained in a separator having two sides; a negative electrode of lithium titanate ( $\text{Li}_4\text{Ti}_5\text{O}_{12}$ ) disposed on one side of the separator; a negative current collector associated with the negative electrode; a positive electrode disposed on an opposite side of the separator; and a positive current collector associated with the positive electrode. The lithium ion battery further includes gas traps to trap gases in the battery, wherein the gas traps include titanium diboride ( $\text{TiB}_2$ ) nanotubes. A method includes providing the titanium diboride nanotubes, carbon nanotubes, carbon fibers, and/or graphene as gas traps in a lithium ion battery having a negative electrode of lithium titanate.

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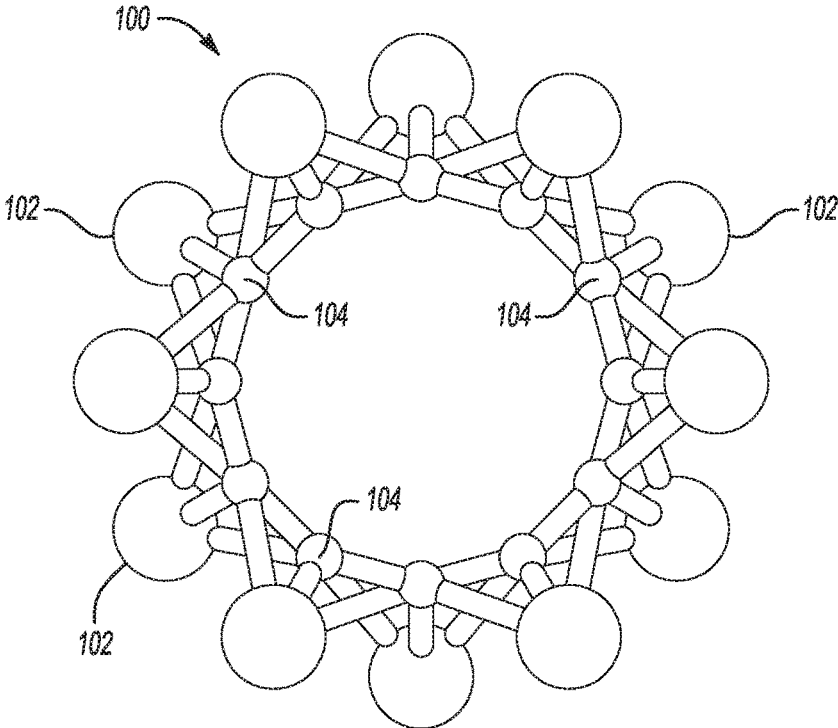


Fig-1A

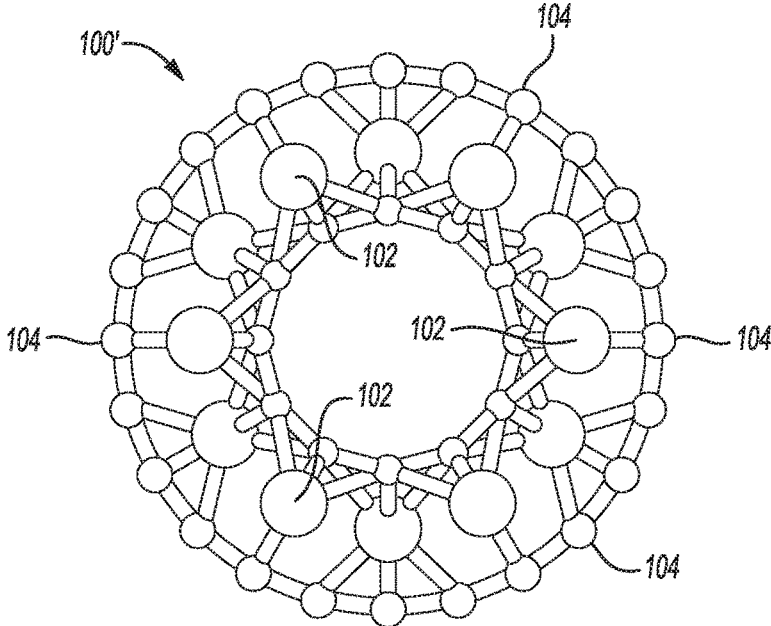


Fig-1B

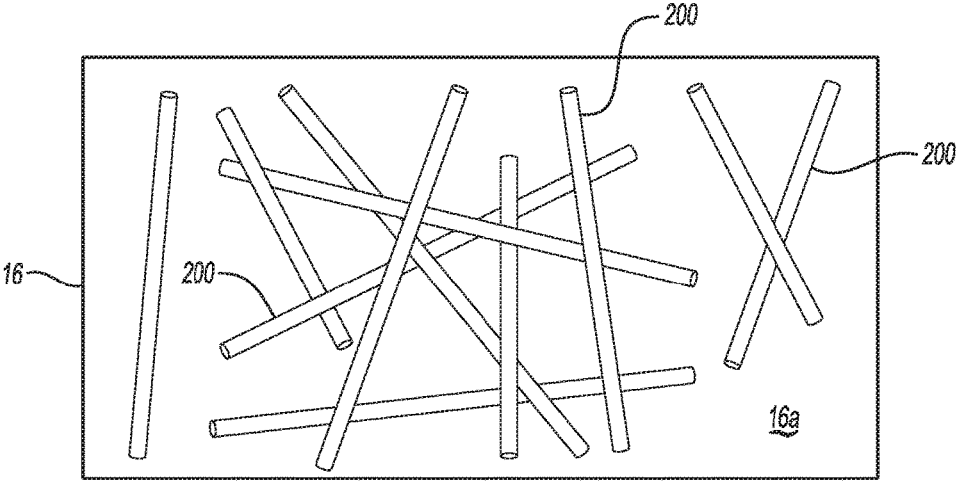


Fig-2

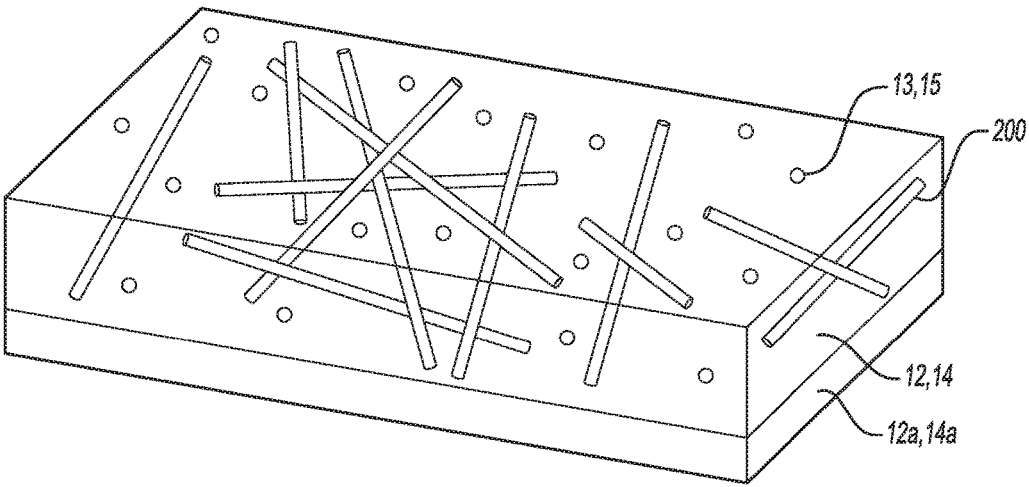


Fig-3

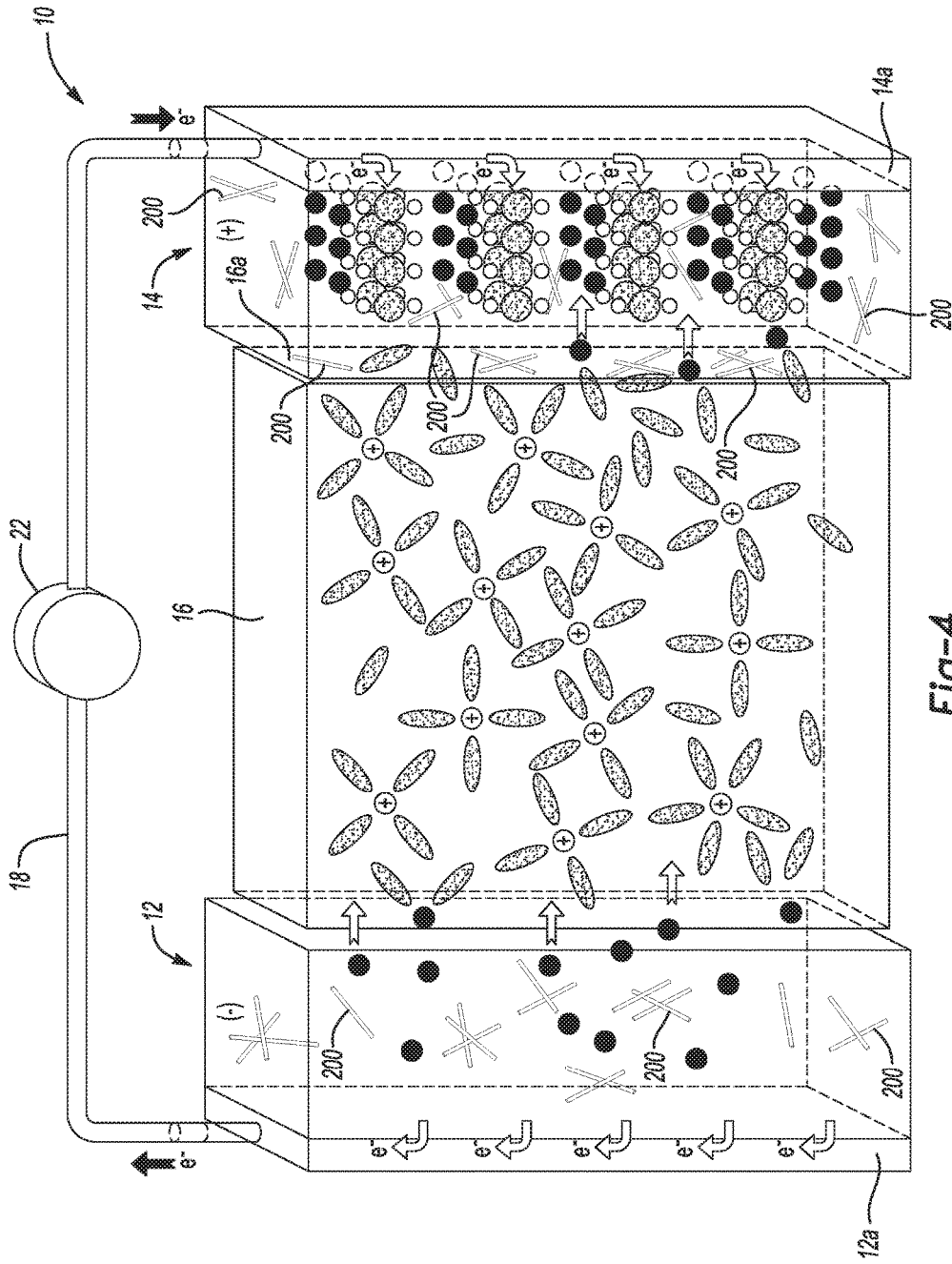


Fig-4

## TITANIUM DIBORIDE NANOTUBES FOR TRAPPING GASES IN LITHIUM ION BATTERIES

### TECHNICAL FIELD

[0001] The present disclosure relates generally to lithium ion batteries, and, in particular to lithium ion batteries in which the negative electrode is lithium titanate.

### BACKGROUND

[0002] Secondary, or rechargeable, lithium ion batteries are used in many stationary and portable devices, such as those encountered in the consumer electronic, automobile, and aerospace industries. The lithium class of batteries has gained popularity for various reasons, including a relatively high energy density, a general non-appearance of any memory effect when compared to other kinds of rechargeable batteries, a relatively low internal resistance, a low self-discharge rate when not in use, and an ability to be formed into a wide variety of shapes (e.g., prismatic) and sizes so as to efficiently fill available space in electric vehicles, cellular phones, and other electronic devices. In addition, the ability of lithium batteries to undergo repeated power cycling over their useful lifetimes makes them an attractive and dependable power source.

### SUMMARY

[0003] A lithium ion battery includes an electrolyte maintained in a separator, the separator having two sides. A negative electrode including a lithium titanate ( $\text{Li}_4\text{Ti}_5\text{O}_{12}$ ) active material is disposed on one side of the separator, and a negative current collector is associated with the negative electrode. A positive electrode is disposed on an opposite side of the separator, and a positive current collector is associated with the positive electrode. The lithium ion battery includes gas traps to trap gases in the battery, wherein the gas traps include titanium diboride ( $\text{TiB}_2$ ) nanotubes. A method includes providing gas traps in a lithium ion battery having a negative electrode including lithium titanate ( $\text{Li}_4\text{Ti}_5\text{O}_{12}$ ), in which the gas traps are titanium diboride ( $\text{TiB}_2$ ) nanotubes, carbon nanotubes, carbon fibers, and/or graphite.

### BRIEF DESCRIPTION OF THE DRAWINGS

[0004] Features of examples of the present disclosure will become apparent by reference to the following detailed description and drawings, in which like reference numerals correspond to similar, though perhaps not identical, components. For the sake of brevity, reference numerals or features having a previously described function may or may not be described in connection with other drawings in which they appear.

[0005] FIGS. 1A and 1B schematically depict an example of a single wall titanium diboride nanotube and a double wall titanium diboride nanotube, respectively.

[0006] FIG. 2 schematically illustrates an example of titanium diboride nanotubes attached to a separator for use in a lithium ion battery.

[0007] FIG. 3 schematically illustrates a perspective view of an example of a generic electrode on a current collector with titanium diboride nanotubes mixed among active material particulates.

[0008] FIG. 4 schematically illustrates an example of a lithium ion battery during a discharging state, wherein both the negative electrode and the positive electrode include the titanium diboride nanotube structures within the respective electrodes and wherein the separator includes the titanium diboride nanotube structures on a surface thereof.

### DETAILED DESCRIPTION

[0009] In some of the examples disclosed herein, a lithium ion battery, having a negative electrode that includes lithium titanate ( $\text{Li}_4\text{Ti}_5\text{O}_{12}$ ) in contact with an electrolyte, is improved by the inclusion of gas traps of titanium diboride ( $\text{TiB}_2$ ) nanotubes. The  $\text{TiB}_2$  nanotubes trap gases generated during operation of the battery.

[0010] A lithium ion battery generally operates by reversibly passing lithium ions between a negative electrode (sometimes called an anode) and a positive electrode (sometimes called a cathode). The negative and positive electrodes are situated on opposite sides of a porous polymer separator that is soaked with an electrolyte solution suitable for conducting lithium ions. Each of the negative and positive electrodes is also accompanied by a respective current collector. The current collectors associated with the two electrodes are connected by an interruptible external circuit that allows an electric current to pass between the electrodes to electrically balance the related migration of lithium ions. Further, the negative electrode may include a lithium insertion host material, such as lithium titanate, and the positive electrode may include an active material that can store lithium ions at a higher electric potential than the lithium insertion host material of the negative electrode.

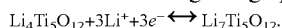
[0011] Briefly, for lithium ion batteries in which the negative electrode (anode) is lithium titanate ( $\text{Li}_4\text{Ti}_5\text{O}_{12}$ , LTO, also called spinel lithium titanate due to its spinel crystal structure), the positive electrode (cathode) may be lithium ion active materials, such as layered lithium transition metal oxides. For example, the lithium ion active material may be spinel lithium manganese oxide ( $\text{LiMn}_2\text{O}_4$ , LMO), lithium nickel manganese cobalt oxide ( $\text{LiNi}_x\text{Co}_y\text{Mn}_{1-x-y}\text{O}_2$ , NMC), lithium cobalt oxide ( $\text{LiCoO}_2$ , LCO), a manganese-nickel oxide spinel [ $\text{Li}(\text{Mn}_{1.5}\text{Ni}_{0.5})\text{O}_2$ , LMNO], lithium iron phosphate ( $\text{LiFePO}_4$ , LFP), or a layered nickel manganese cobalt oxide (having a general formula of  $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2$ , where M is composed of any ratio of Ni, Mn and/or Co). In other examples, the positive electrode may be non-lithium ion active materials, such as metal oxides, including, but not limited to, manganese oxide ( $\text{Mn}_2\text{O}_4$ ), cobalt oxide ( $\text{CoO}_2$ ), a nickel-manganese oxide spinel, a layered nickel manganese cobalt oxide, or an iron polyanion oxide, such as iron phosphate ( $\text{FePO}_4$ ) or iron fluorophosphate ( $\text{FePO}_4\text{F}$ ), or vanadium oxide ( $\text{V}_2\text{O}_5$ ).

[0012] LTO is a particularly desirable negative electrode material. Many Li-based batteries can suffer from capacity fade attributable to many factors, including the formation of a passive film known as a solid electrolyte interphase (SEI) layer over the surface of the negative electrode, which is often generated by reaction products of the negative electrode material, electrolyte reduction, and/or lithium ion reduction. The SEI layer formation plays a significant role in determining electrode behavior and properties including cycle life, irreversible capacity loss, high current efficiency, and high rate capabilities, particularly advantageous for power battery and start-stop battery use. LTO has a high cut voltage (e.g., cut-off potential relative to a lithium metal

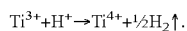
reference potential) that desirably minimizes or avoids SEI formation, and is a zero-strain material having minimal volumetric change during lithium insertion and deinsertion, which enables long term cycling stability, high current efficiency, and high rate capabilities. Such long term cycling stability, high current efficiency, and high rate capabilities are particularly advantageous for power battery and start-stop battery use.

**[0013]** LTO is a promising negative electrode material for high power lithium ion batteries, as described above. However, when used with certain positive electrode materials and electrolytes, LTO may potentially present certain challenges. For example, it has been observed that  $\text{Li}_{4+x}\text{Ti}_5\text{O}_{12}$  can generate significant quantities of gas, which mainly consists of hydrogen, within a battery cell, especially at elevated temperature conditions under a charging state. Such gas formation could make LTO a less desirable choice for commercial use.

**[0014]** Without subscribing to any particular theory, the mechanism for such outgassing appears to be:



In the mechanism,  $\text{Ti}^{4+}$  in  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  is partially reduced to  $\text{Ti}^{4+}/\text{Ti}^{3+}$  in  $\text{Li}_7\text{Ti}_5\text{O}_{12}$ . The  $\text{Ti}^{3+}$  may react with hydrogen ions to form  $\text{Ti}^+$  and hydrogen gas as follows:



Thus, it can be appreciated that outgassing comes, primarily at least, from the generation of hydrogen gas. It is believed that  $\text{Ti}^{3+}$  catalyzes electrolyte reduction reaction to also generate gases such as  $\text{CO}_2$ ,  $\text{CO}$ ,  $\text{N}_2$ , and other gases.

**[0015]** The generation of gases in  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  lithium ion power batteries during operation is a long-standing problem. Previous studies have shown that coatings, such as carbon and metal oxides, can suppress the gassing issue to a certain extent, but cannot solve the problem completely.

**[0016]** The example lithium ion batteries disclosed herein exhibit reduced outgassing. The present inventors have unexpectedly found that titanium diboride ( $\text{TiB}_2$ ) nanotubes can be used as traps to trap hydrogen gas and other gases, where trapping immobilizes the gases to thereby improve the cycle life of high power lithium ion batteries.

**[0017]** In an example of the present disclosure, a lithium ion battery includes an electrolyte maintained in a separator, the separator having two sides. A negative electrode including a lithium titanate ( $\text{Li}_4\text{Ti}_5\text{O}_{12}$ ) active material is disposed on one side of the separator, and a negative current collector is associated with the negative electrode. A positive electrode is disposed on an opposite side of the separator, and a positive current collector is associated with the positive electrode. The lithium ion battery includes gas traps to trap gases in the battery, wherein the gas traps are titanium diboride ( $\text{TiB}_2$ ) nanotubes.

**[0018]** By far, the most significant gas generated in a lithium ion battery is hydrogen ( $\text{H}_2$ , up to about 70 volume percent (vol. %)). The remaining gases, in order of amount generated, include carbon dioxide ( $\text{CO}_2$ , about 20 vol. %), nitrogen ( $\text{N}_2$ , about 5 vol. % to 10 vol. %), and carbon monoxide ( $\text{CO}$ , less than or equal to 5 vol. %).

**[0019]** Since  $\text{TiB}_2$  nanotubes trap hydrogen gas, then a significant portion of the total gases generated in a lithium ion battery are removed or otherwise immobilized. At least some of the remaining gases may also be trapped by  $\text{TiB}_2$  nanotubes. For example, the binding energy of  $\text{TiB}_2$  for  $\text{CO}$  is about 1.43 eV/ $\text{CO}$  molecule (for comparison, the binding

energy of  $\text{TiB}_2$  for  $\text{H}_2$  ranges from about 0.2 to about 0.6 eV/ $\text{H}_2$  molecule). Based on above binding energies,  $\text{TiB}_2$  may trap  $\text{CO}$  as well.

**[0020]**  $\text{TiB}_2$  can form single-walled nanotubes, double-walled nanotubes, and multi-walled (i.e.,  $\geq 3$ ) nanotubes. FIG. 1A is a schematic view of a single-walled  $\text{TiB}_2$  nanotube **100**, showing the arrangement of titanium atoms **102** and boron atoms **104**. FIG. 1B is a schematic view of a double-walled  $\text{TiB}_2$  nanotube **100'**, also showing the arrangement of titanium atoms **102** and boron atoms **104**. A multi-walled  $\text{TiB}_2$  nanotube may have an alternating arrangement of a layer of Ti atoms **102** and a layer of B atoms **104**, based on the double-walled  $\text{TiB}_2$  nanotube **100'** shown in FIG. 1B.

**[0021]** The simplest form of  $\text{TiB}_2$  nanotubes are the single-walled nanotubes **100**, which may be separated from each other. This is because the attraction between two  $\text{TiB}_2$  single-walled nanotubes **100** is weak, with only 0.027 eV/atom at the nearest Ti—Ti distance of 3 Angstroms. Single-walled  $\text{TiB}_2$  nanotubes **100** may be chosen, in some instances, for desirable  $\text{H}_2$  absorption capacity. The inner diameter (i.e., inside diameter) of the single-walled  $\text{TiB}_2$  nanotubes **100** may be within a range of about 2 nm to about 20 nm. The outer diameter (i.e., outside diameter) of the single-walled  $\text{TiB}_2$  nanotubes **100** may be within a range of about 2.6 nm to about 20.6 nm and the length may be within a range of about 50 nm to about 1  $\mu\text{m}$ .

**[0022]** The values for the outside diameter may be determined from the following consideration: if the transformation from single-walled nanotubes **100** to multi-walled nanotubes **100'** occurs (usually the nanotubes are single-walled because of the weak attraction stated above, but sometimes transformation from single-walled to multi-walled does occur), then 2 to 20 layers of  $\text{TiB}_2$  may be formed. As such, the outer diameter of the multi-walled nanotubes **100'** may vary depending upon the number of layers. Each layer may have a thickness of about 3 Angstroms (0.3 nm), and thus the outer diameter of the multi-walled nanotubes **100'** may be within the range of about 2.6 nm to about 20.6 nm.

**[0023]** The  $\text{TiB}_2$  nanotubes may be intentionally included in the lithium ion battery in the negative electrode, or in the positive electrode, or on the separator, or combinations thereof. In the negative electrode, which has lithium titanate ( $\text{Li}_4\text{Ti}_5\text{O}_{12}$ ; LTO) active material, the  $\text{TiB}_2$  nanotubes **100**, **100'** may be present in an amount of about 0.01 weight percent (wt. %) to about 1 wt. %, based on the total weight percent of the LTO active material. Likewise, for the positive electrode and the separator, the  $\text{TiB}_2$  nanotubes may be present in the same concentration range, based on the total weight percent of the LTO active material in the negative electrode **12**.

**[0024]** FIG. 2 depicts a plurality of  $\text{TiB}_2$  nanotubes **200** (which may be single-walled nanotubes **100** and/or multi-walled nanotubes **100'**) lying on a surface **16a** of a separator **16**. The  $\text{TiB}_2$  nanotubes **200** may be adhered to the surface **16a** using any suitable technique. As an example, the technique may involve preparing or otherwise obtaining a dispersion of the nanotubes **200** in a suitable coating material, and then coating the surface **16a** with the dispersion and drying. Examples of coating methods include spray coating and doctor blading.

**[0025]** FIG. 3 depicts a plurality of  $\text{TiB}_2$  nanotubes **200** incorporated within an electrode **12**, **14**. A current collector **12a**, **14a** supports the electrode **12**, **14**, respectively. The

fabrication of electrodes **12**, **14** that incorporate the TiB<sub>2</sub> nanotubes **200** is described in greater detail below. Essentially, the process for forming the electrodes **12**, **14** involves mixing the respective active electrode material **13**, **15** with binder(s) (not shown), conductive agent(s) (not shown), and the nanotubes **200**, and adding a liquid to form a slurry. The slurry is deposited on the current collector **12a**, **14a** and then dried to evaporate the liquid/solvent, leaving behind the mixture of powders that form the electrode **12**, **14**.

[0026] Referring now to FIG. 4, an example of a lithium ion battery **10** is illustrated. The lithium ion battery **10** generally includes negative electrode **12**, negative-side current collector **12a**, positive electrode **14**, positive-side current collector **14a**, and polymer separator **16** disposed between the negative electrode **12** and the positive electrode **14**. An interruptible external circuit **18** connects the negative electrode **12** and the positive electrode **14**. Each of the negative electrode **12**, the positive electrode **14**, and the polymer separator **16** are soaked in an electrolyte solution capable of conducting lithium ions.

[0027] The negative-side current collector **12a** and the positive-side current collector **14a** may be positioned in contact with the negative electrode **12** and the positive electrode **14**, respectively, to collect and move free electrons to and from the external circuit **18**. The negative electrode **12** may be formed directly on the negative-side current collector **12a** and the positive electrode **14** may be formed directly on the positive-side current collector **14a** using the methods disclosed herein. Examples of the current collectors **12a** and **14a** are described below.

[0028] The lithium ion battery **10** may support a load device **22** that can be operatively connected to the external circuit **18**. The load device **22** may be powered fully or partially by the electric current passing through the external circuit **18** when the lithium ion battery **10** is discharging. While the load device **22** may be any number of known electrically-powered devices, a few specific examples of a power-consuming load device include an electric motor for a hybrid vehicle or an all-electrical vehicle, a laptop computer, a cellular phone, and a cordless power tool. The load device **22** may also, however, be a power-generating apparatus that charges the lithium ion battery **10** for purposes of storing energy. For instance, the tendency of windmills and solar panels to variably and/or intermittently generate electricity often results in a need to store surplus energy for later use.

[0029] The lithium ion battery **10** can include a wide range of other components that, while not depicted here, are nonetheless known to skilled artisans. For instance, the lithium ion battery **10** may include a casing, gaskets, terminals, tabs, and any other desirable components or materials that may be situated between or around the negative electrode **12** and the positive electrode **14** for performance-related or other practical purposes. Moreover, the size and shape of the lithium ion battery **10**, as well as the design and chemical make-up of its main components, may vary depending on the particular application for which it is designed. Battery-powered automobiles and hand-held consumer electronic devices, for example, are two instances where the lithium ion battery **10** would most likely be designed to different size, capacity, and power-output specifications. The lithium ion battery **10** may also be connected in series and/or in parallel with other similar lithium ion

batteries to produce a greater voltage output and current (if arranged in parallel) or voltage (if arranged in series) if the load device **22** so requires.

[0030] The lithium ion battery **10** can generate a useful electric current during battery discharge by way of reversible electrochemical reactions that occur when the external circuit **18** is closed to connect the negative electrode **12** and the positive electrode **14** at a time when the negative electrode **12** contains a sufficiently higher relative quantity of lithium insertion/deinsertion material. The chemical potential difference between the positive electrode **14** and the negative electrode **12** (ranging from approximately 1.5V to 5.0V, depending on the exact chemical make-up of the electrodes **12**, **14**) drives electrons produced by the oxidation of lithium titanate at the negative electrode **12** through the external circuit **18** towards the positive electrode **14**. Lithium ions, which are also produced at the negative electrode **12**, are concurrently carried by the electrolyte solution through the polymer separator **16** and towards the positive electrode **14**. The electrons flowing through the external circuit **18** and the lithium ions migrating across the polymer separator **16** in the electrolyte solution eventually reconcile and form inserted lithium at the positive electrode **14**. The electric current passing through the external circuit **18** can be harnessed and directed through the load device **22** until the level of inserted lithium in the negative electrode **12** falls below a workable level or the need for electrical energy ceases.

[0031] The lithium ion battery **10** can be charged or re-powered at any time after a partial or full discharge of its available capacity by applying an external battery charger to the lithium ion battery **10** to reverse the electrochemical reactions that occur during battery discharge. The connection of an external battery charger to the lithium ion battery **10** compels the otherwise non-spontaneous oxidation of, e.g., lithium transition metal oxide at the positive electrode **14** to produce electrons and release lithium ions. The electrons, which flow back towards the negative electrode **12** through the external circuit **18**, and the lithium ions, which are carried by the electrolyte across the polymer separator **16** back towards the negative electrode **12**, reunite at the negative electrode **12** and replenish it with inserted lithium for consumption during the next battery discharge cycle.

[0032] The external battery charger that may be used to charge the lithium ion battery **10** may vary depending on the size, construction, and particular end-use of the lithium ion battery **10**. Examples of some suitable external power sources include a battery charger plugged into an AC wall outlet and a motor vehicle alternator.

[0033] As previously described, the lithium ion battery **10** generally operates by reversibly passing lithium ions between the negative electrode **12** and the positive electrode **14**. In the fully charged state, the voltage of the battery **10** is at a maximum (typically in the range 1.5V to 5.0V); while in the fully discharged state, the voltage of the battery **10** is at a minimum (typically in the range 0V to 2.0V). Essentially, the Fermi energy levels of the active materials in the positive and negative electrodes **14**, **12** change during battery operation, and so does the difference between the two, known as the battery voltage. The battery voltage decreases during discharge, with the Fermi levels getting closer to each other. During charge, the reverse process is occurring, with the battery voltage increasing as the Fermi levels are being driven apart. During battery discharge, the external load

device **22** enables an electronic current flow in the external circuit **18** with a direction such that the difference between the Fermi levels (and, correspondingly, the cell voltage) decreases. The reverse happens during battery charging: the battery charger forces an electronic current flow in the external circuit **18** with a direction such that the difference between the Fermi levels (and, correspondingly, the cell voltage) increases.

**[0034]** At the beginning of a discharge, the negative electrode **12** of the lithium ion battery **10** contains a high concentration of inserted lithium while the positive electrode **14** is relatively depleted. When the negative electrode **12** contains a sufficiently higher relative quantity of inserted lithium, the lithium ion battery **10** can generate a beneficial electric current by way of the previously described reversible electrochemical reactions that occur when the external circuit **18** is closed to connect the negative electrode **12** and the positive electrode **14**. The establishment of the closed external circuit under such circumstances causes the extraction of inserted lithium from the negative electrode **12**. The extracted lithium atoms are split into lithium ions (identified by the black dots and by the open circles having a (+) charge) and electrons ( $e^-$ ) as they leave an insertion host at the negative electrode-electrolyte interface.

**[0035]** The negative electrode **12** includes lithium titanate as the active material **13**. The negative electrode **12** may include the titanium diboride nanotubes **200**, present in an amount ranging from about 0.01 wt. % to about 1 wt. % based on the amount of lithium titanate in the negative electrode **12**. The titanium diboride nanotubes **200** may be distributed throughout the interior of the negative electrode **12**, such as shown with respect to FIGS. **3** and **4**.

**[0036]** The negative electrode **12** may also include conductive filler. The conductive filler may be carbon black or graphite. When included, the carbon black may be present in an amount ranging from about 5 wt. % to about 15 wt. % based on the composition of the negative electrode **12**. The carbon black conductive filler may have a BET surface area greater than 50 m<sup>2</sup>/g. An example of the carbon black conductive filler is SUPER P® (available from Timcal Graphite & Carbon (Bodio, Switzerland)). When included, the graphite may be present in an amount ranging from greater than 0 wt. % to about 3 wt. % based on the composition of the negative electrode **12**. The graphite conductive filler may have D50 of less than 8 μm, and may have a BET surface area ranging from about 5 m<sup>2</sup>/g to about 30 m<sup>2</sup>/g. Commercial forms of graphite that may be used as a conductive filler in the negative electrode **12** are available from, for example, Timcal Graphite & Carbon, Lonza Group (Basel, Switzerland), or Superior Graphite (Chicago, Ill.). One specific example is TIMREX® KS6 (primary synthetic graphite from Timcal Graphite & Carbon).

**[0037]** The negative electrode **12** may also include a binder present in an amount ranging from about 1 wt. % to about 15 wt. % based on the composition of the negative electrode **12**. In an example, the binder is present in an amount ranging from about 2 wt. % to about 8 wt. % based on the composition of the negative electrode **12**. The binder may be polyvinylidene fluoride (PVDF), polytetrafluoroethylene (PTFE), carboxymethylcellulose sodium and polymerized styrene butadiene rubber (CMC+SBR), LA133, or LA132 or combinations thereof. LA133 is an aqueous binder that is a water dispersion of acrylonitrile multi-copolymer and LA132 is an aqueous binder, which is

believed to be a triblock copolymer of acrylamide, lithium methacrylate, and acrylonitrile; both of these acrylonitrile copolymers are available from Chengdu Indigo Power Sources Co., Ltd., Sichuan, P.R.C.

**[0038]** The negative electrode **12** may also include carbon-based materials that serve to trap gases. More particularly, the presence of any of carbon nanotubes, carbon fibers, and graphene in the negative electrode **12**, in addition to TiB<sub>2</sub> nanotubes **200**, may serve to trap gases, such as hydrogen, that are generated during operation of the battery **10**. The carbon nanotubes, carbon fibers, graphene, and titanium diboride (TiB<sub>2</sub> nanotubes **200**) may be used separately or in any combination, within the total concentration of about 0.01 wt. % to about 1 wt. % based on the amount of LTO.

**[0039]** It will be appreciated that H<sub>2</sub> trapping is a physical phenomenon, where surface area of the trap plays a dominant role. As an example, the surface area of any of the gas traps (i.e., TiB<sub>2</sub> or carbon-based material traps) may range from about 500 m<sup>2</sup>/g and 2500 m<sup>2</sup>/g. In an example, the carbon-based material has a single-walled nanotubular shape to maximize the surface area accessible to H<sub>2</sub> and thus maximize H<sub>2</sub> trapping (up to 6.5 wt. %). For example, the carbon nanotubes may have an outer diameter ranging from about 8 nm to about 25 nm and a length ranging from about 0.5 μm to about 20 μm. Likewise, carbon fibers and graphene are suitable as traps because their surface area is strongly dependent on their structure, such as morphologies and dimensions. As such, the morphologies and dimensions may be selected in order to maximize gas trapping. For example, the carbon fibers (such as activated carbon fibers) may be in the form of fibers having a diameter ranging from about 30 nm to about 200 nm, a length ranging from about 0.5 μm to about 10 μm, and a BET surface area ranging from about 1000 m<sup>2</sup>/g to about 2500 m<sup>2</sup>/g. It is to be understood that other carbon fiber dimensions may be utilized to increase the surface area for gas trapping. For another example, a single-layer of graphene up to a few, e.g., 3, layers of graphene also has a large surface area for gas trapping. On the other hand, other forms of carbon that may be used to enhance electrical conductivity, such as graphite, may be unsuitable for trapping H<sub>2</sub> due to the small surface area (e.g., exterior surface only), because the amount of H<sub>2</sub> that can be trapped is limited to a negligible level.

**[0040]** It will be appreciated that the presence of any of the carbon nanotubes, carbon fibers, and graphene in the negative electrode **12**, while serving as gas traps, may also augment the carbon black and/or graphite as conductive filler.

**[0041]** One example of the composition of the negative electrode **12** includes about 80 wt. % lithium titanate, about 10 wt. % graphite, about 10 wt. % PVDF and about 0.08 wt. % TiB<sub>2</sub> (based on 0.1 wt. % of 80 wt. % lithium titanate). In this example, carbon, in the form of nanotubes, carbon fibers, and/or graphene, may be added separately or jointly (instead of or in addition to the TiB<sub>2</sub> nanotubes) in an amount based on 0.1 wt. % of the lithium titanate. It will be appreciated that while carbon is often added to the negative electrode **12** to provide conductivity, carbon nanotubes, carbon fibers, and/or graphene may also trap hydrogen gas, as discussed above.

**[0042]** Adjacent to the negative electrode **12** is the negative-side current collector **12a**, which may be formed from copper or aluminum. In an example, the aluminum may be in the form of bare aluminum foil. The thickness of the



negative-side current collector **12a** may range from about 15  $\mu\text{m}$  to about 25  $\mu\text{m}$ . In another example, the negative-side current collector **12a** may be carbon-coated on at least one side. When the carbon coating is included, the thickness of the carbon coating on one side of the current collector **12a** ranges from about 0.1  $\mu\text{m}$  to about 2  $\mu\text{m}$ .

**[0043]** Additional features of the negative electrode **12** may include: a porosity ranging from about 28% to about 44%; a moisture content less than 700 ppm; an electrical conductivity that is less than  $2 \Omega\text{-cm}$ ; a pressing density (the density after pressing the electrode) ranging from about 1.8  $\text{g/cm}^3$  to about 2.2  $\text{g/cm}^3$ . When the negative electrode **12** is coated on one side of the current collector **12a**, the capacity loading may range from about 0.28  $\text{mAh/cm}^2$  to about 0.84  $\text{mAh/cm}^2$ . The moisture content may be measured by the Karl Fisher method, such as with a C30 Compact Karl Fischer Coulometer, available from Mettler Toledo International, Inc. (Columbus, Ohio).

**[0044]** For lithium ion batteries **10**, the positive electrode **14** may include any suitable active material **15** (FIG. 3) or combinations thereof, present in an amount ranging from about 70 wt. % to about 95 wt. % based on the composition of the positive electrode **14**. More specifically, a common class of known lithium based active materials suitable for this example of the positive electrode **14** includes layered lithium transition metal oxides. For example, the lithium ion active material may be spinel lithium manganese oxide ( $\text{LiMn}_2\text{O}_4$ , LMO), lithium cobalt oxide ( $\text{LiCoO}_2$ ), a manganese-nickel oxide spinel [ $\text{Li}(\text{Mn}_{1.5}\text{Ni}_{0.5})\text{O}_2$ ], or a layered nickel manganese cobalt oxide (having a general formula of  $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2$ , where M is composed of any ratio of Ni, Mn and/or Co). A specific example of the layered nickel-manganese-cobalt oxide includes  $(x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{Li}(\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3})\text{O}_2)$ . Other suitable lithium ion active materials include  $\text{Li}(\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3})\text{O}_2$ ,  $\text{Li}_{x+y}\text{Mn}_{2-y}\text{O}_4$  (LMO,  $0 < x < 1$  and  $0 < y < 0.1$ ), or a lithium iron polyanion oxide, such as lithium iron phosphate ( $\text{LiFePO}_4$ , LFP) or lithium iron fluorophosphate ( $\text{Li}_2\text{FePO}_4\text{F}$ ), or a lithium rich layer-structure. Still other lithium based active materials may also be utilized, such as  $\text{LiNi}_{1-x}\text{Co}_{1-y}\text{M}_{x+y}\text{O}_2$  or  $\text{LiMn}_{1.5-x}\text{Ni}_{0.5-y}\text{M}_{x+y}\text{O}_4$  (M is composed of any ratio of Al, Ti, Cr, and/or Mg), stabilized lithium manganese oxide spinel ( $\text{Li}_x\text{Mn}_{2-y}\text{M}_y\text{O}_4$ , where M is composed of any ratio of Al, Ti, Cr, and/or Mg), lithium nickel cobalt aluminum oxide (e.g.,  $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ ) or NCA), aluminum stabilized lithium manganese oxide spinel (e.g.,  $\text{Li}_x\text{Al}_{0.05}\text{Mn}_{0.95}\text{O}_2$ ), lithium vanadium oxide ( $\text{LiV}_2\text{O}_5$ ),  $\text{Li}_2\text{MSiO}_4$  (where M is composed of any ratio of Co, Fe, and/or Mn), lithium nickel manganese cobalt oxide ( $\text{LiNi}_x\text{Co}_y\text{Mn}_{1-x-y}\text{O}_2$ , NMC), and any other high energy nickel-manganese-cobalt material (HE-NMC). By "any ratio" it is meant that any element may be present in any amount. So, in some examples, M could be Al, with or without Cr, Ti, and/or Mg, or any other combination of the listed elements. In another example, anion substitutions may be made in the lattice of any example of the lithium transition metal based active material to stabilize the crystal structure. For example, any O atom may be substituted with an F atom.

**[0045]** When lithium manganese oxide (LMO) is selected as the active material **15** in the positive electrode **14**, the particle size distribution of the lithium manganese oxide may have D50 of less than 10  $\mu\text{m}$  and D95 of less than 20  $\mu\text{m}$ . In other words, 50% of the lithium manganese oxide particles have a size smaller than 10  $\mu\text{m}$  and 95% of the

lithium manganese oxide particles have a size smaller than 20  $\mu\text{m}$ . The BET surface area of the lithium manganese oxide particles may range from about 0.4  $\text{m}^2/\text{g}$  to about 1.2  $\text{m}^2/\text{g}$ . At a C-rate of 1C, the lithium manganese oxide particles with these specifications exhibit a capacity ranging from about 95  $\text{mAh/g}$  to about 110  $\text{mAh/g}$ .

**[0046]** When lithium nickel manganese cobalt oxide (NMC) is selected as the active material **15** in the positive electrode **14**, the particle size distribution of the lithium nickel manganese cobalt oxide may have D50 of less than 8  $\mu\text{m}$  and D95 of less than 15  $\mu\text{m}$ . In other words, 50% of the lithium nickel manganese cobalt oxide particles have a size smaller than 8  $\mu\text{m}$  and 95% of the lithium nickel manganese cobalt oxide particles have a size smaller than 15  $\mu\text{m}$ . The BET surface area of the lithium nickel manganese cobalt oxide particles ranges from about 0.4  $\text{m}^2/\text{g}$  to about 1.0  $\text{m}^2/\text{g}$ . At a C-rate of 1C, the lithium nickel manganese cobalt oxide particles with these specifications exhibit a capacity ranging from about 135  $\text{mAh/g}$  to about 300  $\text{mAh/g}$ .

**[0047]** The positive electrode **14** may include the titanium diboride nanotubes **200**, present in an amount ranging from about 0.01 wt. % to about 1 wt. % based on the amount of the active material (lithium titanate) in the negative electrode **12**. The titanium diboride nanotubes **200** may be distributed throughout the interior of the positive electrode **14**, such as shown with respect to FIG. 3.

**[0048]** The positive electrode **14** may also include conductive filler, wherein the conductive filler may be carbon black and/or graphite. When included, the carbon black may be present in an amount ranging from about 1 wt. % to about 6 wt. % based on the composition of the positive electrode **14**. The carbon black conductive filler may have a BET surface area greater than 50  $\text{m}^2/\text{g}$ . An example of the carbon black conductive filler is SUPER P® (available from Timcal Graphite & Carbon (Bodio, Switzerland)). When included, the graphite may be present in an amount ranging from greater than 0 wt. % to about 3 wt. % based on the composition of the positive electrode **14**. In an example, the graphite conductive filler has D50 of less than 8  $\mu\text{m}$ , and a BET surface area ranging from about 5  $\text{m}^2/\text{g}$  to about 30  $\text{m}^2/\text{g}$ . Commercial forms of graphite that may be used as a conductive filler in the positive electrode **14** are available from, for example, Timcal Graphite & Carbon (Bodio, Switzerland), Lonza Group (Basel, Switzerland), or Superior Graphite (Chicago, Ill.). One specific example is TIM-REX® KS6 (primary synthetic graphite from Timcal Graphite & Carbon).

**[0049]** The positive electrode **14** may also include a binder present in an amount ranging from about 1 wt. % to about 8 wt. % based on the composition of the positive electrode **14**. In an example, the binder is present in an amount ranging from 1 wt. % to about 5 wt. % based on the composition of the positive electrode **14**. The binder may be any of the same binders listed above, namely, polyvinylidene fluoride (PVDF), polytetrafluoroethylene (PTFE), carboxymethyl-cellulose sodium and polymerized styrene butadiene rubber (CMC+SBR), LA133, or LA132 or combinations thereof.

**[0050]** As with the negative electrode **12**, the presence of any of carbon nanotubes, graphene, and carbon fiber in the positive electrode **14**, in addition to  $\text{TiB}_2$  nanotubes **200**, may serve to trap gases, such as hydrogen, generated during operation of the battery **10**. The carbon nanotubes, carbon fibers, graphene, and titanium diboride ( $\text{TiB}_2$  nanotubes **200**) may be used separately or in any combination, within the

total concentration of about 0.01 wt. % to about 1 wt. % based on the amount of the lithium titanate active material **13**.

**[0051]** One example of the composition of the positive electrode **14** includes about 80 wt. % LMO or NMC, about 10 wt. % graphite, about 10 wt. % PVDF, and about 0.08 wt %  $\text{TiB}_2$  (based on 0.1% of 80 wt % lithium titanate in the negative electrode **12**).

**[0052]** Adjacent to the positive electrode **14** is the positive-side current collector **14a**, which may be formed from aluminum. The thickness of the positive-side current collector **14a** may range from about 15  $\mu\text{m}$  to about 25  $\mu\text{m}$ . In an example, the aluminum may be in the form of foil. In another example, the positive-side current collector **14a** may be carbon-coated on at least one side. When the carbon coating is included, the thickness of the carbon coating on one side of the current collector **14a** ranges from about 0.1  $\mu\text{m}$  to about 2  $\mu\text{m}$ .

**[0053]** Additional features of the positive electrode **14** may include: a porosity ranging from about 25% to about 35% and an electrical conductivity that is less than 2  $\Omega\text{-cm}$ . Where the positive electrode **14** is based on lithium manganese oxide, the moisture content is less than 300 ppm. Where the positive electrode **14** is based on lithium nickel manganese cobalt oxide, the moisture content is less than 500 ppm. Where the positive electrode active material is lithium manganese oxide, then the positive electrode **14** has a pressing density ranging from about 2.5  $\text{g/cm}^3$  to about 2.9  $\text{g/cm}^3$ . Where the positive electrode active material is lithium nickel manganese cobalt oxide, then the positive electrode **14** has a pressing density ranging from about 2.7  $\text{g/cm}^3$  to about 3.1  $\text{g/cm}^3$ . When any example of the positive electrode **14** is coated on one side of the current collector **14a**, the capacity loading may range from about 0.28  $\text{mAh/cm}^2$  to about 0.84  $\text{mAh/cm}^2$ .

**[0054]** The separator **16**, which operates as both an electrical insulator and a mechanical support, is sandwiched between the negative electrode **12** and the positive electrode **14** to prevent physical contact between the two electrodes **12**, **14** and the occurrence of a short circuit. The separator **16**, in addition to providing a physical barrier between the two electrodes **12**, **14**, ensures passage of lithium ions (identified by the black dots and by the open circles having a (+) charge in FIG. 4) and related anions (not shown) through an electrolyte solution filling its pores. This helps ensure that the lithium ion battery **10** functions properly.

**[0055]** The separator **16** may be a microporous polymer separator. The porosity of the separator **16** ranges from about 40% to about 60%. The thickness of the separator **16** ranges from about 10  $\mu\text{m}$  to about 30  $\mu\text{m}$ .

**[0056]** The separator **16** includes, or in some examples is, a membrane, and this membrane may be formed, e.g., from a polyolefin. The polyolefin may be a homopolymer (derived from a single monomer constituent) or a heteropolymer (derived from more than one monomer constituent), and may be either linear or branched. If a heteropolymer derived from two monomer constituents is employed, the polyolefin may assume any copolymer chain arrangement including those of a block copolymer or a random copolymer. The same holds true if the polyolefin is a heteropolymer derived from more than two monomer constituents. As examples, the polyolefin may be polyethylene (PE), polypropylene (PP), a blend of PE and PP, or multi-layered structured porous films of PE and/or PP. Commercially available polyolefin

microporous polymer separators **16** include CELGARD® 2500 (a monolayer polypropylene separator) and CELGARD® 2320 (a trilayer polypropylene/polyethylene/polypropylene separator) available from Celgard LLC. Some other commercially available separators are available from Entek International, Asahi-Kasei Corporation, Toray Industries, and SK Energy.

**[0057]** In another example, the separator **16** may be formed from another polymer chosen from polyethylene terephthalate (PET), polyvinylidene fluoride (PVDF), polyamides (Nylons), polyurethanes, polycarbonates, polyesters, polyetheretherketones (PEEK), polyethersulfones (PES), polyimides (PI), polyamide-imides, polyethers, polyoxymethylene (e.g., acetal), polybutylene terephthalate, polyethylenenaphthenate, polybutene, polyolefin copolymers, acrylonitrile-butadiene styrene copolymers (ABS), polystyrene copolymers, polymethylmethacrylate (PMMA), polyvinyl chloride (PVC), polysiloxane polymers (such as polydimethylsiloxane (PDMS)), polybenzimidazole (PBI), polybenzoxazole (PBO), polyphenylenes (e.g., PARMAX™ (Mississippi Polymer Technologies, Inc., Bay Saint Louis, Miss.)), polyarylene ether ketones, polyperfluorocyclobutanes, polytetrafluoroethylene (PTFE), polyvinylidene fluoride copolymers and terpolymers, polyvinylidene chloride, polyvinylfluoride, liquid crystalline polymers (e.g., VECTRAN™ (Hoechst AG, Germany) and ZENITE® (DuPont, Wilmington, Del.)), polyaramides, polyphenylene oxide, and/or combinations thereof. It is believed that another example of a liquid crystalline polymer that may be used for the membrane of the separator **16** is poly(*p*-hydroxybenzoic acid). In yet another example, the membrane may be a combination of one of these polymers and a polyolefin (such as PE and/or PP).

**[0058]** In yet another example, the membrane of the separator **16** may be chosen from a combination of the polyolefin (such as PE and/or PP) and one or more of the polymers for the separator **16** listed above.

**[0059]** The separator **16** may contain a single layer or a multi-layer laminate fabricated from either a dry or wet process, by solvent casting, by a non-woven fiber laying process, or by any other process for making a microporous polymer membrane with properties suitable for application in Li-ion batteries. For example, a single layer of the polyolefin may constitute the entirety of the separator **16**. In another example, a single layer of one or a combination of any of the polymers from which the separator **16** may be formed (e.g., the polyolefin and/or one or more of the other polymers listed above for the separator **16**) may constitute the entirety of the separator **16**. As another example, however, multiple discrete layers of similar or dissimilar polyolefins and/or polymers for the separator **16** may be assembled into the separator **16**. In one example, a discrete layer of one or more of the polymers may be coated and/or laminated on a discrete layer of the polyolefin for the separator **16**. Further, the polyolefin (and/or other polymer) layer, and any other optional polymer layers, may further be included in the separator **16** as a fibrous layer to help provide the separator **16** with appropriate structural and porosity characteristics. Still other suitable polymer separators **16** include those that have a ceramic layer attached thereto, and those that have ceramic filler in the polymer matrix (i.e., an organic-inorganic composite matrix).

**[0060]** The separator **16** may further have at least one surface **16a** on which the  $\text{TiB}_2$  nanotubes **200** are coated.

The amount of the TiB<sub>2</sub> nanotubes **200** in the coating may be in the same concentration range of 0.01 wt. % to 1 wt. %, based on the total weight percent of the LTO active material in the negative electrode **12**.

[0061] Thus, as noted above, any or all of the negative electrode **12**, the positive electrode **14**, and the separator **16** may include the titanium diboride nanotubes **200**. Further, carbon nanotubes, carbon fibers, and/or graphene may be added, in at least partial, but not total, replacement of the TiB<sub>2</sub> nanotubes **200**.

[0062] Each of the negative electrode **12**, the positive electrode **14**, and the porous separator **16** is soaked in the electrolyte solution. It is to be understood that any appropriate electrolyte solution that can conduct lithium ions between the negative electrode **12** and the positive electrode **14** may be used in the lithium ion battery **10**. In one example, the electrolyte solution may be a non-aqueous liquid electrolyte solution that includes a lithium salt dissolved in an organic solvent or a mixture of organic solvents. Examples of lithium salts that may be dissolved in an organic solvent to form the non-aqueous liquid electrolyte solution include LiClO<sub>4</sub>, LiAlCl<sub>4</sub>, LiI, LiBr, LiSCN, LiBF<sub>4</sub>, LiB(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>, LiCF<sub>3</sub>SO<sub>3</sub>, LiN(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>(LiTFSI), LiN(FSO<sub>2</sub>)<sub>2</sub> (LiFSI), LiAsF<sub>6</sub>, LiPF<sub>6</sub>, LiB(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub> (LiBOB), LiBF<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>) (LiODFB), LiPF<sub>4</sub>(C<sub>2</sub>O<sub>4</sub>) (LiFOP), LiNO<sub>3</sub>, and mixtures thereof. These and other similar lithium salts may be dissolved in a variety of organic solvents such as cyclic carbonates (ethylene carbonate (EC), propylene carbonate (PC), butylene carbonate, fluoroethylene carbonate), linear carbonates (dimethyl carbonate (DMC), diethyl carbonate (DEC), ethylmethyl carbonate (EMC)), aliphatic carboxylic esters (methyl formate, methyl acetate, methyl propionate),  $\gamma$ -lactones ( $\gamma$ -butyrolactone,  $\gamma$ -valerolactone), chain structure ethers (1,2-dimethoxyethane, 1,2-diethoxyethane, ethoxymethoxyethane), cyclic ethers (tetrahydrofuran, 2-methyltetrahydrofuran), and mixtures thereof.

[0063] The electrolyte solution may also include a number of additives, such as solvents and/or salts that are minor components of the solution. Example additives include lithium bis(oxalato borate) (LiBOB), lithium difluoro oxalate borate (LiDFOB), vinylene carbonate, monofluoroethylene carbonate, propane sultone, 2-propyn-ol-methanesulfonate, methyl di-fluoro-acetate, succinic anhydride, maleic anhydride, adiponitrile, biphenyl, ortho-terphenyl, dibenzyl, diphenyl ether, n-methylpyrrole, furan, thiophene, 3,4-ethylenedioxythiophene, 2,5-dihydrofuran, trishexafluoro-iso-propylphosphate, trihydroxybenzene, tetramethoxytitanium, etc. While some examples have been given herein, it is to be understood that other additives could be used. When included, additives may make up from about 0.05% to about 5% of the composition of the electrolyte solution.

[0064] In an example, the electrolyte solution has a conductivity greater than 1.8 mS/cm measured at -30° C.

[0065] The lithium ion battery **10** as disclosed herein has a negative capacity to positive capacity ratio ranging from about 0.9 to about 1.05. The lithium ion battery **10** has an operational temperature ranging from about -30° C. to about 70° C. The lithium ion battery **10** may be in the form of a pouch battery, a prismatic battery, or a cylindrical battery.

[0066] In an example of the method for making the lithium titanate negative electrode **12**, the titanium diboride nanotubes **200** disclosed herein may be mixed with lithium titanate powder (active material **13**), the conductive filler(s),

and the binder(s). In an example of the method for making the positive electrode **14**, any of the previously described active materials **15** may be mixed with the conductive filler(s) and the binder(s). The titanium diboride nanotubes **200** may also be mixed with the active material(s) **15**, the conductive filler(s), and the binder(s).

[0067] For each of the electrodes **12**, **14**, the respective components may be manually mixed by dry-grinding. After all these components are ground together, the ground components are combined with water or organic solvent (depending on the binder used) to form the dispersion/mixture. In an example, the solvent is a polar aprotic solvent. Examples of suitable polar aprotic solvents include dimethylacetamide (DMAC), N-methyl-2-pyrrolidone (NMP), dimethylformamide (DMF), dimethylsulfoxide (DMSO), or another Lewis base, or combinations thereof.

[0068] The dispersion/mixture may be mixed by milling. Milling aids in transforming the dispersion/mixture into a coatable slurry. Low-shear milling or high-shear milling may be used to mix the dispersion/mixture. The dispersion/mixture milling time ranges from about 10 minutes to about 20 hours depending on the milling shear rate. In an example, a rotator mixer is used for about 20 minutes at about 2000 rpm to mill the dispersion/mixture.

[0069] The respective slurry may then be coated or deposited onto the respective current collector **12a**, **14a**. The slurry may be deposited using any suitable technique. As examples, the slurry may be cast on the surface of the current collector **12a**, **14a**, or may be spread on the surface of the current collector **12a**, **14a**, or may be coated on the surface of the current collector **12a**, **14a** using a slot die coater.

[0070] The deposited slurry may be exposed to a drying process in order to remove any remaining solvent and/or water. Drying may be accomplished using any suitable technique. For example, drying may be performed at an elevated temperature ranging from about 60° C. to about 130° C. In some examples, vacuum may also be used to accelerate the drying process. As one example of the drying process, the deposited slurry may be exposed to vacuum at about 120° C. for about 12 to 24 hours. The drying process results in the formation of the negative electrode **12** or the positive electrode **14**.

[0071] The separator **16** may be coated with an appropriate amount of the titanium diboride nanotubes **200**. A coating made up of a suitable adhesive and the TiB<sub>2</sub> nanotubes may be prepared. The coating may then be deposited onto surface **16a** of the separator **16**. Examples of a suitable deposition process include spray coating and doctor blading.

[0072] To further illustrate the present disclosure, examples are given herein. It is to be understood that these examples are provided for illustrative purposes and are not to be construed as limiting the scope of the present disclosure.

## EXAMPLES

### Example 1

[0073] Pouch cells were constructed using lithium titanate (LTO) as the active material for the negative electrode **12** and spinel lithium manganese oxide (LMO) as the active material for the positive electrode **14**. The separator **16** was a microporous tri-layered polypropylene (PP) and polyethylene (PE) polymer membrane, and the electrolyte was 1 M LiPF<sub>6</sub> in a mixed solution of ethylene carbonate and diethyl

carbonate (1:2 volume ratio). The following conditions were followed: 5C charge/10C discharge cycling protocol at 45° C.

**[0074]** The weight of H<sub>2</sub> gas generated in the cell was found to be  $4.51 \times 10^{-5}$  g H<sub>2</sub>/g LTO. Table I shows additional data determined in this Example, in which V is the pouch cell volume.

TABLE I

| Hydrogen Gas Generated in LMO/LTO Cells. |                           |       |                           |  |
|--|---------------------------|-------|---------------------------|--|
| Mass of LTO, g                           |                           | V, ml | Gas Volume, ml            | Calculated H <sub>2</sub> Gas Volume, ml |
| 4.562                                    | Cell 1, after 2000 cycles | 23.1  | 5.7                       |  |
|  | Cell 2, after 2000 cycles | 22.6  | 5.2                       |  |
|  | Cell 3, after 2000 cycles | 21.6  | 4.2                       |  |
|  | Cell before testing       | 17.4  |                           |  |
|  |                           |       | Avg. for cells 1-3 = 5.03 | 2.52                                     |

**[0075]** Before testing, the pouch cell volume was 17.4 ml, and after 2000 cycles, the pouch cell volume increased to 23.1 ml, for example, for Cell 1. So the volume of the generated gas was 23.1–17.4=5.7 ml for Cell 1. The average volume of the generated gas (for the three cells) was  $(5.7+5.2+4.2)/3=5.03$  ml and the pure H<sub>2</sub> was calculated to be  $5.03 \times 50\%$  H<sub>2</sub>=2.52 ml H<sub>2</sub>.

#### Prophetic Example 1

**[0076]** TiB<sub>2</sub> nanotubes exhibit high hydrogen storage of 5.5 wt %. Based on this property, it is possible to calculate the amount of TiB<sub>2</sub> nanotubes needed to completely immobilize H<sub>2</sub> generated in the LTO cell of Example 1. If the total active amount of LTO is 4.562 g (Table I), and if the weight of H<sub>2</sub> gas generated in the cell is  $4.51 \times 10^{-5}$  g H<sub>2</sub>/g LTO (Example 1), then the amount of TiB<sub>2</sub> nanotubes calculated based on 5.5 wt. % H<sub>2</sub> storage is 3.74 mg TiB<sub>2</sub> (0.082 wt. % LTO).

#### Example 2

**[0077]** Pouch cells were constructed using lithium titanate (LTO) as the active material for the negative electrode **12** and lithium nickel manganese cobalt oxide (NMC) as the active material for the positive electrode **14**. The separator **16** was a microporous tri-layered polypropylene (PP) and polyethylene (PE) polymer membrane, and the electrolyte was 1 M LiPF<sub>6</sub> in a mixed solution of ethylene carbonate and diethyl carbonate (1:2 volume ratio). The following conditions were followed: 5C charge/10C discharge cycling protocol at 45° C.

**[0078]** The weight of H<sub>2</sub> gas generated in the cell was found to be  $1.94 \times 10^{-5}$  g H<sub>2</sub>/g LTO. Table II shows additional data determined in this Example.

TABLE II

| Hydrogen Gas Generated in NMC/LTO Cells. |                           |       |                           |  |
|--|---------------------------|-------|---------------------------|--|
| Mass of LTO, g                           |                           | V, ml | Gas Volume, ml            | Calculated H <sub>2</sub> Gas Volume, ml |
| 4.562                                    | Cell 1, after 2000 cycles | 19    | 2.4                       |  |
|  | Cell 2, after 2000 cycles | 18.6  | 2.2                       |  |
|  | Cell 3, after 2000 cycles | 18.7  | 2.1                       |  |
|  | Cell before testing       | 16.6  |                           |  |
|  |                           |       | Avg. for cells 1-3 = 2.17 | 1.08                                     |

#### Prophetic Example 2

**[0079]** Based on the high hydrogen storage property of the TiB<sub>2</sub> nanotubes (5.5 wt % in the nanotubes), it is possible to calculate the amount of TiB<sub>2</sub> nanotubes needed to completely immobilize H<sub>2</sub> generated in the LTO cell of Example 2. If the total active amount of LTO is 4.562 g (Table II), and if the weight of H<sub>2</sub> gas generated in the cell is  $1.94 \times 10^{-5}$  g H<sub>2</sub>/g LTO (Example 2), then the amount of TiB<sub>2</sub> nanotubes calculated based on 5.5 wt. % H<sub>2</sub> storage is 1.61 mg TiB<sub>2</sub> (0.035 wt. % LTO).

**[0080]** It is to be understood that the ranges provided herein include the stated range and any value or sub-range within the stated range. For example, a range from about 100 nm to about 200 nm should be interpreted to include not only the explicitly recited limits of about 100 nm to about 200 nm, but also to include individual values, such as 175 nm, 190 nm, etc., and sub-ranges, such as from about 165 nm to about 185 nm, etc. Furthermore, when “about” is utilized to describe a value, this is meant to encompass minor variations (up to  $\pm 10\%$ ) from the stated value.

**[0081]** Reference throughout the specification to “one example”, “another example”, “an example”, and so forth, means that a particular element (e.g., feature, structure, and/or characteristic) described in connection with the example is included in at least one example described herein, and may or may not be present in other examples. In addition, it is to be understood that the described elements for any example may be combined in any suitable manner in the various examples unless the context clearly dictates otherwise.

**[0082]** In describing and claiming the examples disclosed herein, the singular forms “a”, “an”, and “the” include plural referents unless the context clearly dictates otherwise.

**[0083]** While several examples have been described in detail, it is to be understood that the disclosed examples may be modified. Therefore, the foregoing description is to be considered non-limiting.

#### 1. A lithium ion battery, comprising:

- an electrolyte maintained in a separator, the separator having two sides;
- a negative electrode including a lithium titanate (Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub>) active material disposed on one side of the separator;
- a negative current collector associated with the negative electrode;
- a positive electrode disposed on an opposite side of the separator;

- a positive current collector associated with the positive electrode; and  
gas traps to trap gases in the battery, wherein the gas traps include titanium diboride ( $\text{TiB}_2$ ) nanotubes.
2. The lithium ion battery as defined in claim 1 wherein the  $\text{TiB}_2$  nanotubes are selected from the group consisting of single wall nanotubes, double wall nanotubes, and multi-wall nanotubes.
3. The lithium ion battery as defined in claim 2 wherein the  $\text{TiB}_2$  nanotubes have an outer diameter within a range of about 2.6 nm to about 26 nm, a length within a range of about 50 nm to about 1  $\mu\text{m}$ , and an inside diameter within a range of about 2 nm to about 20 nm.
4. The lithium ion battery as defined in claim 3 wherein the gas traps further include one or more of carbon nanotubes, carbon fibers, and graphene.
5. The lithium ion battery as defined in claim 1 wherein the  $\text{TiB}_2$  nanotubes are in the negative electrode, or in the positive electrode, or on the separator, or combinations thereof.
6. The lithium ion battery as defined in claim 5 wherein the  $\text{TiB}_2$  nanotubes are present within a range of about 0.01 wt. % to about 1 wt. % based on a total wt % of the lithium titanate active material in the negative electrode.
7. A method, comprising:  
providing gas traps in a lithium ion battery having a negative electrode including lithium titanate ( $\text{Li}_4\text{Ti}_5\text{O}_{12}$ ), wherein the gas traps are selected from the group consisting of titanium diboride ( $\text{TiB}_2$ ) nanotubes, carbon nanotubes, carbon fibers, graphene, and combinations thereof.
8. The method as defined in claim 7 wherein the lithium ion battery includes:  
an electrolyte maintained in a separator, the separator having two sides;  
the negative electrode disposed on one side of the separator;  
a negative current collector associated with the negative electrode;  
a positive electrode disposed on an opposite side of the separator; and  
a positive current collector associated with the positive electrode.
9. The method as defined in claim 7 wherein the  $\text{TiB}_2$  nanotubes are selected from the group consisting of single wall nanotubes, double wall nanotubes, and multi-wall nanotubes.
10. The method as defined in claim 9 wherein the  $\text{TiB}_2$  nanotubes have an outer diameter within a range of about 2.6 nm to about 26 nm, a length within a range of about 50 nm to about 1  $\mu\text{m}$ , and an inside diameter within a range of about 2 nm to about 20 nm.
11. The method as defined in claim 10 wherein the gas traps further include one or more of carbon nanotubes, carbon fibers, and graphene.
12. The method as defined in claim 8 wherein the  $\text{TiB}_2$  nanotubes are intentionally included in the negative electrode, or in the positive electrode, or on the separator, or combinations thereof.
13. The method as defined in claim 12 wherein the  $\text{TiB}_2$  nanotubes are present within a range of about 0.01 wt. % to about 1 wt. % based on a total wt % of the lithium titanate in the negative electrode.
14. An improved lithium ion battery having a negative electrode including lithium titanate ( $\text{Li}_4\text{Ti}_5\text{O}_{12}$ ) in contact with an electrolyte, wherein the improvement comprises gas traps to trap gases generated during operation of the battery, wherein the gas traps include titanium diboride ( $\text{TiB}_2$ ) nanotubes.
15. The improved lithium ion battery as defined in claim 14 wherein the lithium ion battery includes:  
the electrolyte maintained in a separator, the separator having two sides;  
the negative electrode disposed on one side of the separator;  
a negative current collector associated with the negative electrode;  
a positive electrode disposed on an opposite side of the separator; and  
a positive current collector associated with the positive electrode.
16. The improved lithium ion battery as defined in claim 15 wherein the  $\text{TiB}_2$  nanotubes are in the negative electrode, or in the positive electrode, or on the separator, or combinations thereof.
17. The improved lithium ion battery as defined in claim 14 wherein the  $\text{TiB}_2$  nanotubes are selected from the group consisting of single wall nanotubes, double wall nanotubes, and multi-wall nanotubes.
18. The improved lithium ion battery as defined in claim 17 wherein the  $\text{TiB}_2$  nanotubes have an outer diameter within a range of about 2.6 nm to about 20.6 nm, a length within a range of about 50 nm to about 1  $\mu\text{m}$ , and an inside diameter within a range of about 2 nm to about 20 nm.
19. The improved lithium ion battery as defined in claim 14 wherein the gas traps further include one or more of carbon nanotubes, carbon fibers, and graphene.
20. The improved lithium ion battery as defined in claim 14 wherein the  $\text{TiB}_2$  nanotubes are present within a range of about 0.01 wt. % to about 1 wt. % based on a total wt % of the lithium titanate.

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