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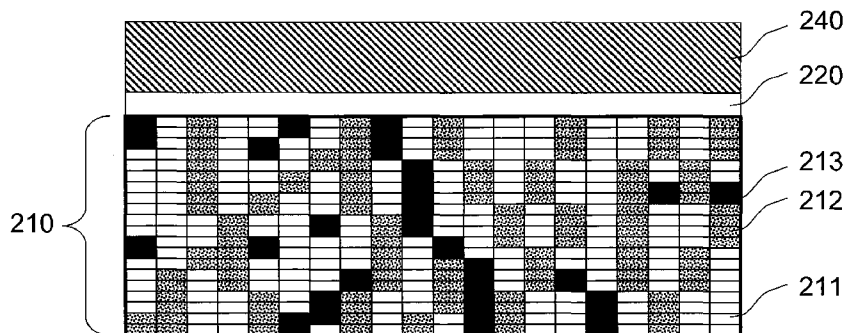


Figure 2

(57) Abstract: Rechargeable, high-density electrochemical devices are disclosed. These electrochemical devices may, for example, include high energy densities that store more energy in a given, limited volume than other batteries and still show acceptable power or current rate capability without any liquid or gel-type battery components. Certain embodiments may involve, for example, low volume or mass of all of the battery components other than the cathode, while simultaneously achieving high electrochemically active mass inside the positive cathode.

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RECHARGEABLE, HIGH-DENSITY ELECTROCHEMICAL DEVICE

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RELATED APPLICATIONS

[0001] The present application claims priority under 35 U.S.C. § 119(e) to U.S. Provisional Application No. 61/352,082, filed June 7, 2010, which is incorporated herein by reference in its entirety.

TECHNICAL FIELD

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[0002] This invention relates to rechargeable, high-density electrochemical devices. In particular, certain embodiments of the present invention relate to, for example, all-solid state, rechargeable batteries with high energy densities that have the capacity to store more energy in a limited volume and still show acceptable power or current rate capability without any liquid or gel-type battery components.

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BACKGROUND OF THE INVENTION

[0003] The capacity of rechargeable and non-rechargeable batteries is defined by the positive cathode and the negative anode. When using a metallic lithium anode (*e.g.* in Li-MnO₂ coin cells) or a capacity rich Li-ion anode that, for example, may be based on silicon or tin, the capacity of the battery is dominated or limited by the specific capacity (measured in mAh/g or mAh/ccm) of the positive cathode. Reducing the volume of all of the other battery components, which is most useful for small batteries, or the mass of all of the other battery components, which is most useful for large batteries (*e.g.* in electric vehicles), while simultaneously increasing the electrochemically active mass inside the positive cathode is the most effective approach to increase the energy density (measured in Wh/liter, for example) of a battery for a given cathode-anode chemistry.

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[0004] Increasing the electrochemically active mass inside the positive cathode means to either reduce any auxiliary phases inside the cathode, such as mechanical binders or ionic or electronic conduction enhancers, or fabricate the cathode thicker for a given cathode area. Due to the limiting diffusion kinetics and the associated limited current rate or power capability when the cathode thickness becomes substantial ($\gg 20\mu\text{m}$), high energy density room temperature batteries, such as cell phone and laptop batteries, require a highly

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conductive, liquid-organic-solvent based lithium ion electrolyte to penetrate the cathodes of these batteries. However, the presence of the liquid organic solvent is the origin of most problems experienced with such batteries over the last twenty years such as, for instance, thermal runaway upon decomposition or short-circuiting of the battery upon heat-related failure, fire/fume/smoke/explosion upon certain battery failure modes, gas evolution and pressure build-up in the early electrochemical cycles, charge-discharge cycle limitation to 300-1000 cycles, limited operational temperature range (0°C – 60°C in many cases), among others. In addition, constraining the volatile liquid organic solvent demands specific packaging architectures and cell housing often equipped with vents and valves that avoid cell over-pressurization during the early electrochemical cycles.

[0005] There is a need in the industry for batteries with higher energy densities. In particular, there is a need for all-solid-state rechargeable batteries without any liquid or gel-type battery components to store more energy in a limited volume that still show acceptable power and/or current rate capability. This results in a safer battery and allows for the use of simplified packaging and higher and lower temperature ranges of operation and storage.

SUMMARY OF INVENTION

[0006] Certain exemplary embodiments of this invention may include batteries with high energy density for a given cathode-anode chemistry. Certain embodiments, as discussed in further detail below, may involve, for example, low volume or mass of all of the battery components other than the cathode, while simultaneously achieving high electrochemically active mass inside the positive cathode.

[0007] An embodiment of a rechargeable electrochemical device with a positive composite cathode may include a solid-state electrochemically active material, a solid-state electronically conducting material which has an electronic conductivity that is at least three times higher than the electronic conductivity of said electrochemically active material before the electrochemically active material is initially charged, and a solid-state, inorganic, ionically conducting material which has an ionic conductivity that is at least three times higher than the ionic conductivity of said electrochemically active material before the electrochemically active material is initially charged.

[0008] Alternatively, an embodiment of a rechargeable electrochemical device with a positive composite cathode may include at least one solid-state electrochemically active

material, at least one solid-state, ionically conducting material that is different from the electrochemically active material, and may not contain liquid or gel-like solvent.

[0009] An alternative embodiment of a rechargeable electrochemical device may include a solid state positive cathode, a negative anode, and a solid state electrolyte sandwiched between the cathode and the anode; wherein the electrochemical device contains a single electrochemical cell which has a rated capacity preferably of, for example, at least 2mAh/cm² based on the geometric footprint of the positive cathode.

BRIEF DESCRIPTION OF THE DRAWINGS

[0010] Figure 1 illustrates a cross-sectional view of an exemplary Li-ion or Li-polymer battery that could be used in a cell phone.

[0011] Figure 2 illustrates an exemplary electrochemical device with three solid phases including an electrochemically active cathode material, an ionic conductivity enhancer and an electronic conductivity enhancer.

[0012] Figure 3 illustrates an exemplary electrochemical device with two solid phases including an electrochemically active cathode material and an electronic conductivity enhancer.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

[0013] It is to be understood that the present invention is not limited to the particular methodology, compounds, materials, manufacturing techniques, uses, and applications described herein, as these may vary. It is also to be understood that the terminology used herein is used for the purpose of describing particular embodiments only, and is not intended to limit the scope of the present invention. It must be noted that as used herein and in the appended claims, the singular forms “a,” “an,” and “the” include the plural reference unless the context clearly dictates otherwise. Thus, for example, a reference to “an element” is a reference to one or more elements, and includes equivalents thereof known to those skilled in the art. Similarly, for another example, a reference to “a step” or “a means” is a reference to one or more steps or means and may include sub-steps or subservient means. All conjunctions used are to be understood in the most inclusive sense possible. Thus, the word “or” should be understood as having the definition of a logical “or” rather than that of a logical “exclusive or” unless the context clearly necessitates otherwise. Structures described herein are to be understood also to refer to functional equivalents of such structures.

Language that may be construed to express approximation should be so understood unless the context clearly dictates otherwise.

[0014] Unless defined otherwise, all technical and scientific terms used herein have the same meanings as commonly understood by one of ordinary skill in the art to which this invention belongs. Preferred methods, techniques, devices and materials are described
5 although any methods, techniques, devices, or materials similar or equivalent to those described may be used in the practice or testing of the present invention. Structures described herein are to be understood also to refer to functional equivalents of such structures.

[0015] All patents and other publications are incorporated herein by reference for the purpose of describing and disclosing, for example, the methodologies described in such
10 publications that might be useful in connection with the present invention. These publications are provided solely for their disclosure prior to the filing date of the present application. Nothing in this regard should be construed as an admission that the inventors are not entitled to antedate such disclosure by virtue of prior invention or for any other reason.

[0016] Certain embodiments of the present invention, for example, include an all-solid state, high energy density battery cell that does not contain any liquid or gel-like components, unlike traditional cell phone batteries and coin cells. Gel-like components consist of, for example, solvents that have viscosities so high they do not flow like a common liquid. The high energy density may be accomplished through a combination of features,
15 such as, for example:

1. maximizing the cathode thickness per unit cathode area while keeping the charge and discharge current capability within acceptable performance limits;
2. optimizing the loading or volume percentage of the electrochemically active mass inside the cathode, which may include a composite rather than a single phase of
25 electrochemically active material to make up 100% of the cathode volume;
3. utilizing a composite electrochemically active material which contains all-solid state lithium ion conduction and electron conduction enhancing phases; and/or
4. minimizing the volume fraction of all of the other battery cell components, such as the substrate, electrolyte, negative anode, current collectors and terminals and the
30 packaging.

Regarding item 1, certain embodiments of the present invention, for example, may include an electrochemical device with a cathode thickness of about 100 – 1000 μ m, whereas the cathode thickness of cell phone type batteries may be, for example, approximately 100 μ m. Regarding item 2, an example electrochemical device may preferably use a loading of the

5 electrochemically active material of higher than about 50 vol%. To enhance the power and current rate capability of the cell (items 1 and 3), the remaining, for instance, 50 vol% of the composite cathode may be filled with two materials: (a) a lithium ion conduction enhancing material, which is chemically stable with the electrochemically active cathode material during fabrication and battery operation and storage while showing an ionic conductivity that is at

10 least three times higher than that of the electrochemically active material; and (b) an electron conduction enhancing material which has an electronic conductivity that is at least three times higher than that of the electrochemically active material. Regarding item 4, the device of certain embodiments of the present invention may be configured, among other parts, with:

15 (i) a thin metal cathode current collector, such as, for instance, 10 μ m Al foil, which also serves as an optional substrate (or no such current collector if the positive cathode is conductive enough along its outside surface to which the positive terminal may be connected); (ii) a thin-film electrolyte, such as, for instance, 1-3 μ m thick Lipon; and (iii) a thin metal anode, such as, for instance, 10 – 50 μ m of metallic lithium. One or more elements of item 4 may be fabricated into the device of certain embodiments of the present invention

20 by physical vapor deposition (PVD) processing or heat-pressure lamination using readily available Li foil. Finally, the device of certain embodiments of the present invention may be, for example, packaged using a thin-film encapsulation of about 3 μ m in thickness, as previously disclosed, for example, in U.S. Pat. Appl. Pub. No. 2009/0181303, which is incorporated herein by reference in its entirety.

25 [0017] In certain embodiments, the absence of any volatile liquid organic solvents inside the composite cathode and/or the electrolyte can be highly conducive to improved safety and higher temperature limits for operation and storage of the electrochemical device, which include lead-free solder reflow conditions during which temperature excursions of up to 265°C may occur for several minutes.

30 [0018] Lower cost versions of a high-capacity cell of certain embodiments of the present invention may include electrolyte alternatives comprising a thicker ceramic layer, or multi-layers, that are entirely or partially fabricated by non-PVD or non- chemical vapor deposition (CVD) methods, such as traditional ceramic or wet chemical processing.

Examples of these electrolyte alternatives may include compacted $\text{Li}_2\text{S-SiS}_2$ or $\text{Li}_2\text{S-P}_2\text{S}_5$ based glass electrolyte powder ($\sim 100\mu\text{m}$ layer thickness), $\text{Li}_3\text{N - LiTi}_2(\text{PO}_4)_3$ dual layer ceramic plate ($\sim 100\mu\text{m}$ thickness), single-sided Lipon protected $\text{LiAl}_2\text{Ti}(\text{PO}_4)_3$ or $\text{Li}_{0.35}\text{La}_{0.55}\text{TiO}_3$ plates ($\sim 100\mu\text{m}$ thickness) or compacted (pressed) $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ powder
5 ($\sim 50\mu\text{m}$ thickness). Analogous to the composite cathode, a composite anode may be used for certain embodiments of the present invention and may include ceramic compacted, Li_ySn -activated, nano-sized $\text{Li}_4\text{Ti}_5\text{O}_{12}$ powder (1.5V vs. Li^+/Li ; results include 1.5V voltage reduction of the fully fabricated electrochemical cell of certain embodiments of the present invention when compared to those 4V cells that employ a metal lithium anode) wherein Li_ySn
10 serves as a lithium ion and electron conduction enhancing second phase in the volume unchanging $\text{Li}_x\text{Ti}_5\text{O}_{12}$ ($4 \leq x \leq 7$) anode phase. Other composite anodes may also be employed.

[0019] Although the fabrication of solid state, high capacity cells with ceramic and/or wet chemistry fabricated electrolytes and/or anodes may be attractive because of their cost and manufacturing throughput, they do not include the power and energy density
15 performance of the cells according to certain embodiments of the present invention that use a thin-film electrolyte and a metal anode consisting entirely of the electrochemically active species of the cell (such as metallic lithium for Li-ion batteries). These lower cost batteries are less desirable because the ceramic and/or wet chemistry fabricated electrolyte and/or composite anode are typically thicker (which may increase cell resistance and add non-energy
20 containing volume to cell, both of which are undesirable characteristics) and provide lower cell voltages (which may cause lower energy and lower power, both of which are undesirable characteristics).

[0020] Good cathode performance for certain embodiments of the present invention (for both pure cathodes and composite cathodes) may require, for example, a high, effective
25 diffusion coefficient inside the cathode. Such a diffusion coefficient inside the cathode allows for, upon cell discharge, as many electrochemically active species (ions and electrons) as possible to be inserted into the cathode in the shortest time possible and into cathode locations that are farthest away from the diffusion originating plane, which is the cathode-electrolyte interface. In a simplified picture, one may use the one-dimensional solution of
30 Fick's second law of diffusion wherein for a given diffusion coefficient, D , a wave-front of diffusing species penetrates a body after a diffusion period t by depth X (sometimes called diffusion length) according to

$$X = 2 (D * t)^{1/2} \quad (1)$$

[0021] Equation (1) is an accurate estimate for the combined diffusion of ions and electrons. In many practical electrochemically active cathode materials, the electronic conductivity is much higher than that of the electrochemically active ions. For example, the electronic conductivity in charged Li_xCoO_2 ($x < 0.7$) is about 1 S/cm at ambient temperatures while that of the lithium ions is less than 10^{-7} S/cm. Therefore, it may be beneficial to enhance the lithium ion conductivity of the cathode by admixing appropriate lithium ion conduction enhancing materials, thereby forming a cathode composite.

[0022] In certain embodiments, using the ionic conductivity as the determining, independent variable for equation (1), the diffusion coefficient D may be replaced by part of Fick's law of diffusion, which is

$$D = RT/(c * z * F^2 * dE/dx) * j \quad (2)$$

that relates D to the gas constant R , the absolute temperature T , the local concentration of diffusing species c , the charge number z of these species ($z = 1$ for Li^+ ions), the Faraday constant F , the local electric field strength dE/dx , and the current density j of the diffusing species. The resulting equation after inserting equation (2) into equation (1) and squaring both sides of the resulting equation is

$$X^2 = 4 * RT/(c * z * F^2 * dE/dx) * t * j \quad (3)$$

wherein the diffusion period t could also be interpreted as the continuous discharge or charge time that it takes at a given current density j to discharge or charge the rated capacity of a cathode wherein the rated capacity is proportional to the thickness X of the cathode for a given cathode composition of electrochemically active cathode material, ionic conductivity enhancing material and electronic conductivity enhancing material. The rated capacity of a cathode is, for example, the discharge capacity of a battery supplied at ambient conditions following a full battery charge. The resulting equation after converting the current density j into the conductivity G using Ohm's law with resistance R and voltage E across the entire cathode, which in turn has the cross-sectional diffusion area A ,

$$R = E / (j * A) \quad (4)$$

and the definition for the conductivity G (= inverse resistivity)

$$G = 1/R * X/A \quad (5)$$

is

$$j = E * G / X \quad (6)$$

10

The resulting equation after inserting equation (6) into equation (2) and considering the voltage drop across the entire thickness X of the cathode is

$$X^2 = 4 * RT / (c * z * F^2 * dE/dX) * t * E * G / X \quad (7)$$

15

or, after rearranging equation (7),

$$X^3 = 4 * RT / (c * z * F^2 * dE/dX) * t * E * G \quad (8)$$

20

For a constant electric field gradient throughout the cathode, which may be the case for electronically well conducting cathodes, dE/dx becomes E/X such that equation (8) simplifies to

$$X^2 = 4 * RT / (c * z * F^2) * t * G \quad (9)$$

25

Therefore,

$$X^2 \sim t * G \quad (10)$$

30

[0023] Equation (10) may be considered a design rule for cathodes if, for example, for a given diffusion period (or discharge or charge time) t through thickness X of an electrochemical cell, the ionic conductivity G of the cathode may be increased four-fold before one may afford to double the thickness X of the cathode in order to double its capacity

per footprint under otherwise constant parameters (*i.e.*, the same electrochemically active material, same volumetric loading of electrochemically active material, same cross-sectional area of the cathode, among others). The discharge time capability of batteries may be given its reciprocal value, the so-called C-rate, which defines how often a battery or
 5 electrochemical cell is able to mathematically discharge its rated capacity in one hour when mathematically neglecting the charge periods in between discharges.

[0024] Equation (10) also represents that for a given conductivity G inside the cathode, increasing the cathode thickness can cause a much slower (*i.e.*, longer) discharge time capability (lower C-rate). For example, the discharge time for full discharge of a given
 10 rated capacity may increase approximately four-fold (C-rate drops to about 25%) when doubling the thickness of the cathode. Maintaining a given rated capacity while doubling the cathode thickness implies that the thickness increase can be accomplished either by adding electrochemical inert material to the cathode, doubling its porosity or changing the electro-
 active material inside the cathode.

[0025] Equation (10) further teaches that adding electrochemically inert material to the cathode, such as mere ionic or electronic conductivity enhancers that do not store electrochemical capacity or energy and therefore merely increase the thickness of the cathode by ΔX without increasing the capacity or energy of the cathode, comes with a price: it
 15 therefore may be appropriate in certain embodiments to add the inert material if it may increase the ionic conductivity of the (composite) cathode to $G * (X + \Delta X)^2 / X^2$ in order to
 20 maintain or, even better, shorten the discharge or charge time because

$$(X + \Delta X)^2 \sim t * G [(X + \Delta X)^2 / X^2] \quad (11)$$

[0026] The importance of, and need for, a great ionic conductivity inside certain
 25 embodiments of the cathode is evident. Since the electrochemically active cathode material such as, for instance, commercially available LiCoO_2 , may not provide a sufficiently high lithium ion conductivity itself (*e.g.*, it may exhibit at ambient temperatures $<10^{-7}$ S/cm throughout its electrochemically active range between 4.2V – 2.0V vs. Li^+ / Li) one may, for
 30 instance, fabricate composite cathodes with lithium ion conductivity enhancing materials which have a lithium ion conductivity that is substantially higher than that of the electrochemically active cathode material.

[0027] After the selection of appropriate lithium ion conduction enhancing material, such as, for example, lithium lanthanum titanate ($\text{Li}_{0.35}\text{La}_{0.55}\text{TiO}_3$ has $G = 10^{-3}$ S/cm (bulk) and $G = 2 * 10^{-5}$ S/cm (grain boundary) at 25°C , an example of which is discussed in Y. Inaguma et al., Solid State Communications 86 (1993) p.689, which is incorporated herein by reference in its entirety), lithium lanthanum zirconate ($\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ exhibits $7.7 * 10^{-4}$ S/cm at 25°C , an example of which is discussed in R. Murugan et al., Angewandte Chemie International Edition 46 (2007) 7778, which is incorporated herein by reference in its entirety), lithium aluminum titanium, phosphate ($\text{Li}_{1.3}\text{Ti}_{1.7}\text{Al}_{0.3}(\text{PO}_4)_3$ shows $7 * 10^{-4}$ S/cm at 25°C , an example of which is discussed in G. Adachi et. al, U.S. Pat. No. 4,985,317, which is incorporated herein by reference in its entirety), or lithium thio-phosphate (80 at% $\text{Li}_2\text{S} - 20$ at% P_2S_5 [= $\text{Li}_8\text{P}_2\text{S}_9$; “Thio-LISICON II”] shows $7.4 * 10^{-4}$ S/cm at 25°C , an example of which is discussed in Senga Minoru et. al, U.S. Pat. Appl. Publ. No. 2007/0160911, which is incorporated herein by reference in its entirety), it is important in certain circumstances to ensure that the morphology, which comprises particle size and particle size distribution, of the lithium ion conductivity enhancing material is tuned to the particle size and distribution of the electrochemically active cathode material inside the composite cathode. This approach may provide a positive three-dimensional network of lithium ion conductivity inside said composite cathode. Porosity within the composite cathode may offset the effectiveness of materials with great conductivity (applies to ions and electrons) due to poor conduction paths or inter-grain contact area, which in turn may be maximized for optimum conduction between the grains and throughout the composite cathode. This objective may be well accomplished with particle sizes preferably in the range of approximately $0.1 - 10\mu\text{m}$, and most preferably $0.5 - 5\mu\text{m}$, for both the ionic conductivity enhancing material and the electrochemically active material within the cathode. Much larger particles than $10\mu\text{m}$ may entail the risk of shadowing or interrupting the ionic conduction path in the ionic network and also the electron conduction path in the electronic network.

[0028] Alternatively or additionally, the ionic conductivity of the electrochemically active material itself may be enhanced. This may be achieved by, for example, doping its bulk grain (intra-grain) portion with other, appropriate chemical elements and/or by chemically or mechanically modifying its grain boundaries, which may be the premier ionic conduction gateways between the grains inside a solid state cathode. Chemical modification via reaction with appropriate chemicals may be a preferred method according to certain embodiments of the present invention. Fast ionic grain boundary conduction is most effective

in providing ions to and from the locations of the electrochemical reactions responsible for capacity and energy storage, which are inside the grain bulk. If the so-enhanced electrochemically active material in grain bulk and/or grain boundary, for example LiCoO_2 , inside the cathode shows a sufficiently high lithium ion conductivity, then the addition of an inert phase that merely provides enhanced lithium ion conductivity, such as, for instance, lithium lanthanum titanate ($\text{Li}_{0.35}\text{La}_{0.55}\text{TiO}_3$), may become unnecessary. However, it may be important to ensure that the cathode is electronically conducting well, for example with an electronic conductivity that is much higher than the lithium ion conductivity inside the cathode. Otherwise, the electronic conductivity of the cathode may limit the effectiveness of the lithium ion conductivity, and thus the lithium diffusion through the cathode may occur only at the pace of the limiting electronic conductivity, according to equation (9) when applying to electrons instead of ions.

[0029] Electron conductivity enhancing materials are relatively inexpensive such as, for example, carbon or nickel powder. These materials are fairly stable up to at least 500°C with commonly used electrochemically active materials (*e.g.*, LiCoO_2) and selected ionic conductivity enhancing materials, such as, for example, lithium lanthanum titanate ($\text{Li}_{0.35}\text{La}_{0.55}\text{TiO}_3$) or lithium lanthanum zirconate ($\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$). It is preferred according to certain embodiments of the present invention to have these electronic conductivity enhancing materials available in an appropriate particle size distribution that is conducive to maximizing the electronic conductivity of the composite cathode, most preferably at the lowest admixed volume fraction of electron conductivity enhancing material. If one used larger particles, such as, for example, $50\mu\text{m}$ Ni, then these particles may provide the composite cathode with a good electronic conductivity but may unnecessarily remove valuable volume inside the composite cathode that may not be filled with the more important electrochemically active cathode material (which provides energy) and/or the optional lithium ion conductivity enhancing material (may enhance the power capability at that energy level).

[0030] Alternatively or additionally, the electronic conductivity of the electrochemically active material itself may be enhanced. This may be achieved by, for example, doping its bulk grain (intra-grain) portion with other, appropriate chemical elements and/or by chemically or mechanically modifying its grain boundaries, which may be the premier electronic conduction gateways between the grains inside a solid state cathode. Chemical modification via reaction with appropriate chemicals may be a preferred method according to certain embodiments of the present invention. Fast electronic grain boundary

conduction is most effective in providing electrons to and from the locations of the electrochemical reactions responsible for capacity and energy storage, which are inside the grain bulk. If the so-enhanced electrochemically active material in grain bulk and/or grain boundary, for example LiCoO_2 , inside the cathode shows a sufficiently high electronic conductivity, then the addition of an inert phase that merely provides enhanced electronic conductivity without supplying substantial electrochemical storage capacity in the positive cathode, such as, for instance, nickel or carbon powder, may become unnecessary.

[0031] Appropriate particle sizes and distribution may be generated using, for example, high energy ball milling that may grind raw powders down to nano/sub-micron sized particles. Specific particle size distribution of a given material could be accomplished by mixing separately ground powder batches for which different grinding parameters were applied. Since the so-obtained powder of one material (*e.g.*, the lithium ion conductivity enhancing material) has a specific particle size distribution, this powder may be mixed with another material (*e.g.*, the electrochemically active cathode material) that has a particle size distribution that has been created in a similar fashion. Finally, the electron conductivity enhancing material (specific particle size distribution made in a similar manner as employed for the lithium ion conductivity enhancing material) may be added to the powder mix. Then, homogenizing the powder mix may be achieved in various ways, such as, for example, by low-energy ball milling using low concentrations of low-density grinding media such as Si_3N_4 or Al_2O_3 , which may or may not further change the particle size distribution of one or more materials within the powder mixture.

EXAMPLE EMBODIMENTS OF THE PRESENT INVENTION

[0032] Example 1: According to an embodiment of the present invention, a commercially available LiCoO_2 powder may be used to determine its electronic conductivity at ambient conditions prior to its initial charge by (a) cold pressing 7 tons of a 0.5mm thick and 10mm in diameter powder pellet, which may achieve 76% of the theoretical density of 5.06 g/ccm and (b) by cold pressing 7 tons of 0.5mm thick and 10mm in diameter powder pellet followed by sintering the pellet at 900°C for 1h in air, which may achieve 72% of the theoretical density of 5.06 g/ccm. The so-obtained pellets may then be coated with 0.3µm thick, PVD fabricated, lithium ion blocking gold electrodes on both pellet faces and subjected

to electronic resistance measurements using electrochemical impedance spectroscopy and 10mV of amplitude. The electronic conductivity of an exemplary cold pressed LiCoO₂ pellet obtained $2.7 * 10^{-5}$ S/cm while the pellet that may be annealed at 900°C exhibited an electronic conductivity of $7.1 * 10^{-4}$ S/cm.

5 **[0033]** Example 2: According to an embodiment of the present invention, the electronic conductivity of a commercially available Ni powder (2-3μm grain size) may be determined from a cold pressed a 7 ton Ni pellet that was 0.5mm thick and 10mm in dia.. The density may be 80% of the theoretical density (8.91 g/ccm). The so-obtained Ni pellet may be sandwiched between two copper electrodes and subjected to 10mVDC. However, the
10 electronic resistance may be so low ($\ll 1$ Ohm) that the currents fall outside the capability of the test equipment (10A). Instead of determining the exact electronic conductivity, the electronic conductivity may be approximated by the literature value for Ni, which at 25°C is about 10^5 S/cm. This value is more than 10 orders of magnitude greater than that of LiCoO₂ prior to the initial charge.

15 **[0034]** Example 3: According to an embodiment of the present invention, the commercially available LiCoO₂ powder from Example 1 may be used to determine its ionic conductivity at ambient conditions prior to its initial charge by (a) cold pressing 7 tons of a 0.5mm thick and 10mm in diameter powder pellet and by (b) cold pressing 7 tons of a 0.5mm thick and 10mm in diameter powder pellet followed by sintering of the pellet at 700°C for 1h
20 in air, which may achieve 73% of the theoretical density of 5.06 g/ccm. The so-obtained pellets may be coated with a 3μm thick electron blocking Lipon electrolyte layer on each pellet face. In addition, two metallic Li electrodes may be PVD fabricated onto the Lipon electrolyte layers opposite to the sandwiched LiCoO₂ pellet. This ionic conductivity test cell may be subjected to ohmic resistance measurements by applying various voltages between 1
25 – 5 VDC to the lithium electrodes whereupon lithium plating or stripping may occur. In this setup, only lithium ions may conduct through the LiCoO₂ pellet while its electronic conduction was completely arrested. The resulting, instant currents may show ohmic behavior and were calculated into resistances. Subtracting the known, combined resistances of the two 3μm Lipon layers connected in series (from other separate experiments) enabled
30 the extraction of the ionic conductivity of LiCoO₂ prior to its initial charge. The ionic conductivity of both an exemplary cold pressed LiCoO₂ pellet and the cold pressed LiCoO₂ pellet that was subsequently annealed at 700°C for 1h in air was $2 * 10^{-8}$ S/cm when measured at 25°C, which is more than three orders of magnitude lower than the electronic

conductivity of LiCoO_2 at 25°C . Therefore, LiCoO_2 in this example demonstrates a predominantly electronically conducting material with a poor lithium ion conductivity.

[0035] Example 4: According to an embodiment of the present invention, $\text{Li}_{0.35}\text{La}_{0.55}\text{TiO}_3$ may be synthesized by standard powder reaction from the starting compounds LiOH , La_2O_3 , and TiO_2 . The final powder, $\text{Li}_{0.35}\text{La}_{0.55}\text{TiO}_3$, may be virtually free of impurity phases as verified by XRD. This powder may then be (a) cold pressed a 7 ton, 0.4mm thick and 10mm diameter powder pellet, which achieved 64% of the theoretical density of 4.99 g/ccm, and (b) cold pressed a 7 ton, 0.4mm thick and 10mm diameter powder pellet and subsequently sintered at 1100°C for 1h in air, which may achieve 70% of the theoretical density of 4.99 g/ccm. The so-obtained pellets may be applied with a PVD fabricated gold electrode on each pellet face. The ionic conductivity of the $\text{Li}_{0.35}\text{La}_{0.55}\text{TiO}_3$ pellets may be determined by electrochemical impedance spectroscopy that can reveal a grain boundary (inter-grain) conductivity of $5.6 * 10^{-8}$ S/cm measured at 25°C for the cold pressed pellet while the bulk (intra-grain) conductivity may not be determined due the limited frequency capability of the test setup, which in turn may require frequencies of about 10 MHz range. The grain boundary conductivity of $\text{Li}_{0.35}\text{La}_{0.55}\text{TiO}_3$ pellets annealed at 700°C for 1h in air was determined to about $1.8 * 10^{-7}$ S/cm when measured at 25°C . The 1100°C fabricated pellet, however, may allow the deconvolution into bulk (inter-grain) and grain boundary (intra-grain) conductivity, which can amount to $5.6 * 10^{-4}$ S/cm and $2.4 * 10^{-6}$ S/cm, respectively. These conductivities may be more than two orders of magnitude larger than the lithium ion conductivity of LiCoO_2 prior to its initial charge (see Example 3).

[0036] Example 5: According to an embodiment of the present invention, a composite cathode may be fabricated with, for example, a mixture of 80 wt% LiCoO_2 and 20 wt% Ni without the addition of an ionic conduction enhancer such as $\text{Li}_{0.35}\text{La}_{0.55}\text{TiO}_3$. The mixture may be cold pressed into a composite cathode pellet of the dimensions 0.3mm x 10mm in diameter. Other pellets may be further treated by sintering the pellets at 700°C for 1h in air. The resulting cold pressed or sintered composite cathode pellets may remain electronically well conducting ($>10^{-2}$ S/cm). When fabricated into full electrochemical cells comprising 1.5 μm thick Lipon electrolyte and a 10 μm metal Li anode, both pellet types may be found to suffer from severe current rate limitations as early as during the initial charge step at a constant voltage of 4.2V. At 25°C the current may decay to about 1 μA within minutes, which may cause charge times of more than 10,000 h (more than 1 year) in the case of a 10mAh cell. Such a cell, for example, may contain 83 mg of LiCoO_2 . The mere composition of

electrochemically active cathode material (LiCoO_2), which exhibits ionic and electronic conductivities sufficient, for example, for small cathode thicknesses, such as, for example, less than $30\mu\text{m}$, which are routinely built in thin-film form in certain embodiments of the present invention. Furthermore, electronic conduction enhancer (Ni) may not lead to
 5 electrochemically well active composite cathodes when used in substantial thicknesses ($\gg 30\mu\text{m}$) for high capacity cells ($> 1\text{mAh}/\text{cm}^2$). Therefore, at least one critical component may be missing from the composite cathode to attain useful battery performance.

[0037] Example 6: This example demonstrates an exemplary potential improvement over Example 5. According to an embodiment of the present invention, the powders used
 10 from Examples 1 – 4 may be mixed in the following weight percentage ratio: 40 wt% LiCoO_2 (theoretical density = 5.06 g/ccm), 40 wt% $\text{Li}_{0.35}\text{La}_{0.55}\text{TiO}_3$ (theoretical density = 4.99 g/ccm), and 20 wt% Ni (theoretical density = 8.91 g/ccm). The powder mixture may be cold pressed into a 0.3mm x 10mm in diameter composite cathode pellet of 80% of the theoretical density, which may be calculated from equation (12):

15

$$\text{Theoretical density of composite cathode pellet (g/ccm)} = 100\% / (40 \text{ wt}\% / 5.06 \text{ g/ccm} + 40 \text{ wt}\% / 4.99 \text{ g/ccm} + 20 \text{ wt}\% / 8.91 \text{ g/ccm}) = 5.50 \text{ g/ccm} \quad (12)$$

The electronic conductivity of an exemplary composite cathode pellet using two sandwiching
 20 copper plates was greater than 10^{-2} S/cm while no new phases were detected by XRD other than the starting constituents LiCoO_2 , $\text{Li}_{0.35}\text{La}_{0.55}\text{TiO}_3$, and Ni. The ionic conductivity of the composite cathode may be estimated from the volume fraction of the $\text{Li}_{0.35}\text{La}_{0.55}\text{TiO}_3$ within the composite cathode, which is given by equation (13):

25

$$\text{vol}\% \text{ of } \text{Li}_{0.35}\text{La}_{0.55}\text{TiO}_3 = 40 \text{ wt}\% * 5.50 \text{ g/ccm} / 4.99 \text{ g/ccm} = 44 \text{ vol}\% \quad (13)$$

In a first approximation it may be assumed that pellet the following approximation holds true inside the composite cathode:

30

$$\text{Density of composite cathode} / \text{actual density of } \text{Li}_{0.35}\text{La}_{0.55}\text{TiO}_3 \approx \text{theoretical density of composite cathode} / \text{theoretical density of } \text{Li}_{0.35}\text{La}_{0.55}\text{TiO}_3 \quad (14)$$

so that equation (13) provides a good estimate for the actual vol% of $\text{Li}_{0.35}\text{La}_{0.55}\text{TiO}_3$ inside the composite cathode. It may be further assumed that the lithium ion conductivity for an ideal grain size composition inside the composite cathode may be determined by the vol% of the dominant lithium ion conductor according to

5

$$\text{Actual vol\% Li}_{0.35}\text{La}_{0.55}\text{TiO}_3 * 5.6 * 10^{-8} \text{ S/cm} = 2.5 * 10^{-8} \text{ S/cm} \quad (15)$$

[0038] This lithium ion conductivity, example, based on the lithium ion grain boundary conductivity of $\text{Li}_{0.35}\text{La}_{0.55}\text{TiO}_3$ when cold pressed into a composite cathode pellet and not further heat treated, may be too low for practical purposes and may be similar to
10 lithium ion conductivity of pure LiCoO_2 (see Example 3). Therefore, the composite cathode pellet may be heat treated at 700°C at which the composite cathode may be provided with $0.44 * 1.8 * 10^{-7} \text{ S/cm} = 7.9 * 10^{-8} \text{ S/cm}$. This may still not be enough lithium ionic conductivity for practical applications (see Example 14). Annealing the composite cathode
15 pellet at 900°C may cause some reaction of LiCoO_2 with Ni to form NiO and LiCoO_2 decomposition side phases. The improvement in lithium ion conductivity may be minor and/or may rise to about $4 * 10^{-7} \text{ S/cm}$.

[0039] It may be evident that the lithium ionic grain boundary conductivity of the enhancer material can be improved when inside the composite cathode. The composite
20 cathode may, for example, not be processed above a certain temperature (*e.g.*, 900°C) before undesirable chemical reactions can set in between the constituents of the composite cathode.

[0040] These certain exemplary improvements may be accomplished by grinding and milling the powder of the lithium ion conductivity enhancer to smaller grain sizes ($<2\mu\text{m}$) and/or by appropriately modifying its grain surfaces, mechanically or chemically, to increase
25 its lithium ion grain boundary conductivity. This so-surface-modified lithium ion conductivity enhancer material may exhibit a grain boundary conductivity of about 10^{-4} S/cm when cold pressed into composite cathode pellets and followed by an anneal step at 700°C for 1h in air. An overall lithium ion conductivity of an exemplary composite cathode of about 10^{-4} S/cm may permit continuous current draws of C/30, which translates into 0.2mA for
30 6mAh cells, which may have a $300\mu\text{m}$ thick composite cathode (see Example 13).

[0041] Example 7: According to an embodiment of the present invention, a 10mm diameter electrochemical cell providing 2 mAh/cm^2 capacity based on the geometric footprint of the positive cathode may be fabricated with a composite cathode consisting of 40 wt%

LiCoO₂ (theoretical density = 5.06 g/ccm), 40 wt% Li_{0.35}La_{0.55}TiO₃ (theoretical density = 4.99 g/ccm), and 20 wt% Ni (theoretical density = 8.91 g/ccm). The geometric footprint of a cathode is, for example, the surface area that one obtains when looking onto a surface along its surface normal or along the main axis of a device which has a geometric area that is measured while assuming a perfectly smooth surface. With this loading of the electrochemical active cathode material (LiCoO₂) the composite cathode can be fabricated with 11.2 mg LiCoO₂ thereby leading to a thickness, preferably of about $28 \text{ mg} / (0.785 \text{ cm}^2 * 80\% * 5.50 \text{ g/ccm}) = 81 \text{ }\mu\text{m}$.

[0042] Example 8: According to an embodiment of the present invention, a 10mm diameter electrochemical cell providing 2 mAh/cm² capacity may be fabricated with a composite cathode consisting of 20 wt% LiCoO₂ (theoretical density = 5.06 g/ccm), 60 wt% Li_{0.35}La_{0.55}TiO₃ (theoretical density = 4.99 g/ccm), and 20 wt% Ni (theoretical density = 8.91 g/ccm). With this loading of the electrochemical active cathode material (LiCoO₂), the composite cathode can be fabricated with 11.2 mg LiCoO₂, thereby leading to a thickness of about $56 \text{ mg} / (0.785 \text{ cm}^2 * 80\% * 5.49 \text{ g/ccm}) = 162 \text{ }\mu\text{m}$.

[0043] Example 9: According to an embodiment of the present invention, a 10mm diameter electrochemical cell providing 4 mAh/cm² capacity may be fabricated with a composite cathode consisting of 40 wt% LiCoO₂ (theoretical density = 5.06 g/ccm), 40 wt% Li_{0.35}La_{0.55}TiO₃ (theoretical density = 4.99 g/ccm), and 20 wt% Ni (theoretical density = 8.91 g/ccm). With this loading of the electrochemical active cathode material (LiCoO₂), the composite cathode can be fabricated with 22.4 mg LiCoO₂, thereby leading to a thickness of about $56 \text{ mg} / (0.785 \text{ cm}^2 * 80\% * 5.50 \text{ g/ccm}) = 162 \text{ }\mu\text{m}$.

[0044] Example 10: According to an embodiment of the present invention, a 10mm diameter electrochemical cell providing 4 mAh/cm² capacity may be fabricated with a composite cathode consisting of 20 wt% LiCoO₂ (theoretical density = 5.06 g/ccm), 60 wt% Li_{0.35}La_{0.55}TiO₃ (theoretical density = 4.99 g/ccm), and 20 wt% Ni (theoretical density = 8.91 g/ccm). With this loading of the electrochemical active cathode material (LiCoO₂), the composite cathode can be fabricated with 22.4 mg LiCoO₂, thereby leading to a thickness of about $112 \text{ mg} / (0.785 \text{ cm}^2 * 80\% * 5.49 \text{ g/ccm}) = 325 \text{ }\mu\text{m}$.

[0045] Example 11: According to an embodiment of the present invention, a 10mm diameter electrochemical cell providing 5 mAh/cm² capacity may be fabricated with a composite cathode consisting of 40 wt% LiCoO₂ (theoretical density = 5.06 g/ccm), 40 wt% Li_{0.35}La_{0.55}TiO₃ (theoretical density = 4.99 g/ccm), and 20 wt% Ni (theoretical density = 8.91

g/ccm). With this loading of the electrochemical active cathode material (LiCoO₂), the composite cathode can be fabricated with 28 mg LiCoO₂, thereby leading to a thickness of about $70 \text{ mg} / (0.785 \text{ cm}^2 * 80\% * 5.50 \text{ g/ccm}) = 203 \text{ }\mu\text{m}$.

[0046] Example 12: According to an embodiment of the present invention, a 10mm diameter electrochemical cell providing 5 mAh/cm² capacity may be fabricated with a composite cathode consisting of 20 wt% LiCoO₂ (theoretical density = 5.06 g/ccm), 60 wt% Li_{0.35}La_{0.55}TiO₃ (theoretical density = 4.99 g/ccm), and 20 wt% Ni (theoretical density = 8.91 g/ccm). With this loading of the electrochemical active cathode material (LiCoO₂), the composite cathode can be fabricated with 28 mg LiCoO₂, thereby leading to a thickness of about $140 \text{ mg} / (0.785 \text{ cm}^2 * 80\% * 5.49 \text{ g/ccm}) = 406 \text{ }\mu\text{m}$.

[0047] Example 13: According to an embodiment of the present invention, the cell of Example 11 wherein the 28 mg of LiCoO₂ material may be replaced by 28 mg of Li_{1.2}Ni_{0.175}Co_{0.10}Mn_{0.525}O₂ (see, e.g., U.S. Pat. Appl. Publ. No. 2010/086853, which is incorporated herein by reference in its entirety), which may improve the capacity of the cell by 70% when cycled between 4.6 – 2.0V and while concomitantly enhancing the capacity per unit area from 5 mAh/cm² to more than approximately 8.5 mAh/cm². Since the theoretical densities of LiCoO₂ and Li_{1.2}Ni_{0.175}Co_{0.10}Mn_{0.525}O₂ are similar, the actual densities of the fabricated composite cathode pellets in the cells are also similar, and therefore both composite cathode pellet thicknesses may be approximately 200μm.

[0048] Example 14: According to an embodiment of the present invention, after rearranging equation (9),

$$X^2 = 4 * RT / (c * z * F^2) * t * G \quad (16)$$

25 to

$$X^2 * c * z * F^2 / (4 * RT) = t * G \quad (17)$$

wherein

30

c = vol% of active cathode loading in composite cathode *
 concentration of mobile ionic species in the given active cathode
 material (18)

For the case wherein the active cathode material is LiCoO_2 , $c = \text{vol}\%$ of active cathode loading in composite cathode $\times 2.3 \times 10^{-2} \text{ mol/ccm}$ (100% dense composite cathode assumed), $z = 1$, $F = 96485 \text{ C/mol}$, $R = 8.3143 \text{ J/(K} \cdot \text{mol)}$, $T = 298 \text{ K}$, and

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$$(\text{Thickness of composite cathode})^2 \times \text{vol}\% \text{ active cathode loading in composite cathode} \times 2.2 \times 10^4 \text{ sec}/(\text{Ohm} \cdot \text{ccm}) = \text{discharge time} \times \text{lithium ion conductivity in composite cathode} \quad (19)$$

10 **[0049]** In the case of a $500\mu\text{m}$ thick composite cathode with a 40 vol% loading, for example, a 10 hours (36,000 sec) discharge or charge time (C/10 rate) requires a minimum lithium ion conductivity inside the composite cathode of about $6 \times 10^{-4} \text{ S/cm}$ while a C/30 rate (30 hours discharge time or charge time) demands only about $2 \times 10^{-4} \text{ S/cm}$.

15 **[0050]** Doubling the cathode loading (80 vol% active loading), for example, while maintaining a given capacity allows the composite cathode to be fabricated in about $\frac{1}{2}$ the cathode thickness or $250\mu\text{m}$. As a result, the C/10 rate capability may require only about $3 \times 10^{-4} \text{ S/cm}$ while the C/30 scenario may only need about $1 \times 10^{-4} \text{ S/cm}$.

20 **[0051]** Because creating composite cathodes with high lithium ion conductivity at, for example, 10^{-4} S/cm , is difficult, one option, for a given capacity in a given composite cathode and for a given discharge or charge time at a given temperature, may be to maximize the vol% loading of the active electrochemical material inside the composite cathode while concurrently minimizing the thickness of the composite cathode.

25 **[0052]** For a given capacity Q in the given composite cathode which has a given ionic conductivity, the discharge or charge time t determines the maximum continuous discharge or charge current according to

$$\text{maximum continuous discharge or charge current} = Q / t \quad (20)$$

30 **[0053]** Example 15: According to an embodiment of the present invention, a cell similar to the cell in example 7, but in which the $\text{Li}_{0.35}\text{La}_{0.55}\text{TiO}_3$ powder has an average grain size of less than $2\mu\text{m}$, may have an improved grain boundary conductivity in a manner that it enables the cell to be continuously discharged to about 2 mAh/cm^2 within 10 hours or less within its reversibility range of 4.2 – 2.0V. Reversibility range is, for example, the

commonly accepted voltage range within which a given electrode is “substantially” stable at a given temperature. Higher temperatures may typically reduce reversibility range of electrodes. For example, at 25°C, the reversibility range of LiCoO₂ is commonly accepted as 4.2 – 2.0V vs. Li⁺/Li, which is equivalent to a stoichiometry range from about Li_{1.0}CoO₂ (2.0V vs. Li⁺/Li) to about Li_{0.5}CoO₂ (4.2V vs. Li⁺/Li).

5 [0054] Example 16: According to an embodiment of the present invention, a cell similar to the cell in example 9, but in which the Li_{0.35}La_{0.55}TiO₃ powder has an average grain size of less than 1μm, may have an improved grain boundary conductivity that enables the cell to be continuously discharged to about 4 mAh/cm² within 10 hours or less within 4.2 – 10 2.0V.

[0055] Example 17: According to an embodiment of the present invention, a cell similar to the cell in example 11, but in which the Li_{0.35}La_{0.55}TiO₃ powder has an average grain size of less than 0.5μm, which may have an improved grain boundary conductivity that enables the cell to be continuously (and fully) discharged to about 5 mAh/cm² in 10 hours or 15 less within 4.2 – 2.0V.

[0056] Example 18: According to an embodiment of the present invention, the electrochemical cell of Example 7 may be configured with a 1.5μm thick Lipon electrolyte, a 10μm thick metal Li anode, a 10μm Al cathode current collector foil, a 10μm Cu anode current collector foil and a polymeric pouch encapsulation of 100μm wall thickness above 20 and below the electrochemical cell. Such characteristics provide a volumetric capacity density (which is calculated, for example, by dividing the rated capacity by the fully packaged battery volume) of about 59 Ah/liter in a fully packaged state and a volumetric energy density (which is calculated, for example, by dividing the product of rated capacity times the rated voltage by the fully packaged battery volume) of about 236 Wh/liter, after 25 taking into account that the Li anode increases its thickness to a total of about 22μm and the composite cathode to a total of about 82μm when the cell is charged to 4.2V. A “fully packaged state”, for example, is the state of a battery that includes all of the peripherals inherent to the battery, which includes, for example, current collectors, terminals, primary encapsulation (if the housing is not already included in the encapsulation), and the housing.

30 [0057] Example 19: According to an embodiment of the present invention, the electrochemical cell of Example 9 may be configured with a 1.5μm thick Lipon electrolyte, a 10μm thick metal Li anode, a 10μm Al cathode current collector foil, a 10μm Cu anode current collector foil, and a polymeric pouch encapsulation of 100μm wall thickness above

and below the electrochemical cell. Such characteristics provide a volumetric capacity density of about 92 Ah/liter in a fully packaged state and a volumetric energy density of about 368 Wh/liter, after taking into account that the Li anode increases its thickness to a total of about 34 μ m and the composite cathode to a total of about 163 μ m when the cell is charged to 4.2V.

[0058] Example 20: According to an embodiment of the present invention, the electrochemical cell of Example 11 may be configured with a 1.5 μ m thick Lipon electrolyte, a 10 μ m thick metal Li anode, a 10 μ m Al cathode current collector foil, a 10 μ m Cu anode current collector foil, and a polymeric pouch encapsulation of 100 μ m wall thickness above and below the electrochemical cell. Such characteristics provide a volumetric capacity density of about 103 Ah/liter in a fully packaged state and a volumetric energy density of about 412 Wh/liter, after taking into account that the Li anode increases its thickness to a total of about 40 μ m and the composite cathode to a total of about 205 μ m when the cell is charged to 4.2V.

[0059] Example 21: According to an embodiment of the present invention, the energy densities given in Examples 18, 19, and 20 increase to about 354 Wh/liter, about 552 Wh/liter, and about 618 Wh/liter, respectively, when increasing the loading of the electrochemically active cathode material (LiCoO₂) in each example from about 40 wt% to about 60 wt% and reducing the lithium conductivity enhancing material (Li_{0.35}La_{0.55}TiO₃, which has very similar density as LiCoO₂ so that that the thickness of the composite cathode remains virtually the same) from about 40 wt% to about 20 wt%.

[0060] Example 22: According to an embodiment of the present invention, a 618 Wh/liter cell from Example 21 contains about 5.89 mAh and may be configured with a 50 μ m thick Li₇La₃Zr₂O₁₂ electrolyte, a 50 μ m thick Li_ySn-activated, a nano-sized Li₄Ti₅O₁₂ Li-ion anode, a 10 μ m Al cathode current collector foil, a 10 μ m Cu anode current collector foil, and polymeric pouch encapsulation of 100 μ m wall thickness above and below the electrochemical cell. This configuration provides the cell with a volumetric capacity density of about 135 Ah/liter in a fully packaged state and a volumetric energy density of about 338 Wh/liter, while the anode thickness remains approximately constant at about 50 μ m and the composite cathode may reach a total thickness of about 205 μ m when the cell is charged to 4.2V. The midpoint voltage, however, may change from 4.0V (Example 21) to about 2.5V.

[0061] Example 23: According to an embodiment of the present invention, a composite cathode may be fabricated consisting of a mixture of 60 wt% LiCoO₂, 20 wt% Ni,

and 20 wt% of chemically surface modified $\text{Li}_{0.35}\text{La}_{0.55}\text{TiO}_3$. The chemical surface modification of $\text{Li}_{0.35}\text{La}_{0.55}\text{TiO}_3$ may be accomplished by separate and prior reaction with $\text{LiIO}_4 \cdot 2\text{H}_2\text{O}$, Polypyrrole, Li_3N , Ni or carbon at temperatures between $250^\circ\text{C} - 900^\circ\text{C}$. The mixture may then be cold pressed into a composite cathode pellet of the dimensions 0.3mm x 10mm in diameter and subsequently annealed at $250^\circ\text{C} - 500^\circ\text{C}$ for 1h in air. The resulting annealed composite cathode pellets remains electronically well conducting ($>10^{-2}$ S/cm). When fabricated into full electrochemical cells comprising 1.5 μm thick Lipon electrolyte and a 10 μm metal Li anode, the composite cathode may supply the cell with continuous charge and discharge currents greater than C/30 of between 4.2 – 2.0V. The chemical surface modification substantially enhances the lithium ion conductivity of the ionic conductivity enhancer material ($\text{Li}_{0.35}\text{La}_{0.55}\text{TiO}_3$) by about three orders of magnitude from a lithium ion grain boundary (intra-grain) conductivity of 10^{-7} S/cm to a lithium ion grain boundary conductivity value close to 10^{-4} S/cm.

[0062] Example 24: According to an embodiment of the present invention, a composite cathode consisting of a mixture of about 80 wt% chemically surface modified LiCoO_2 and about 20 wt% Ni without the addition of any ionic conduction enhancer such as $\text{Li}_{0.35}\text{La}_{0.55}\text{TiO}_3$ may be fabricated. The chemical surface modification of LiCoO_2 may be accomplished by separate and prior reaction with $\text{LiIO}_4 \cdot 2\text{H}_2\text{O}$ or Polypyrrole at temperatures between about $250^\circ\text{C} - 900^\circ\text{C}$. The mixture may then be cold pressed into a composite cathode pellet of the dimensions 0.3mm x 10mm in diameter and subsequently annealed at about $250^\circ\text{C} - 500^\circ\text{C}$ for 1h in air. The resulting annealed composite cathode pellets may remain electronically well conducting ($>10^{-2}$ S/cm). When fabricated into full electrochemical cells comprising 1.5 μm thick Lipon electrolyte and a 10 μm metal Li anode, these composite cathodes in these cells may sustain continuous charge and discharge currents greater than C/30 of between 4.2 – 2.0V. It is evident that the chemical surface modification substantially enhances the lithium ion conductivity of the electrochemically active material (LiCoO_2) by more than approximately 3 orders of magnitude from about $2 \cdot 10^{-8}$ S/cm to a value close to about 10^{-4} S/cm. This approach allows the fabrication of composite cathodes, which have an ionic conductivity enhancer that may be the electrochemically active material itself, thereby rendering a separately provided ionic conductivity enhancer that has no electrochemical storage capacity (e.g., $\text{Li}_{0.35}\text{La}_{0.55}\text{TiO}_3$) redundant.

[0063] Example 25: According to an embodiment of the present invention, a 10mm diameter electrochemical cell that utilizes the composite cathode from Example 24 may be

fabricated. The composite cathode may have an actual cold pressed density of about 4.43 g/ccm, which is about 80% of its theoretical density of about 5.54 g/ccm, and a thickness of about 350 μ m. This composite cathode supplies the cell with about 13.7mAh of capacity. This cell may be further configured with a 1.5 μ m thick Lipon electrolyte, a 10 μ m thick metal Li
5 anode, a 10 μ m Al cathode current collector foil, a 10 μ m Cu anode current collector foil and polymeric pouch encapsulation of 100 μ m wall thickness above and below the electrochemical cell. This construction provides the cell with a volumetric capacity density of about 254 Ah/liter in a fully packaged state and a volumetric energy density of about 1018 Wh/liter, after taking into account that the Li anode will increase its thickness to a total of
10 about 92 μ m and the composite cathode to a total of about 355 μ m when the cell is charged to 4.2V. Such an electrochemical cell may have an improved grain boundary conductivity that enables the cell to be continuously (and fully) discharged to about 17 mAh/cm² in 10 hours or less within 4.2 – 2.0V.

[0064] Figure 1 shows a prior art cross-sectional view of a Li-ion or Li-polymer
15 battery as used in cell phone batteries. The composite cathode 110 is typically approximately 100 μ m thick and composed of four phases, three of which are solid state phases and the fourth of which is a liquid phase. The electrochemically active cathode material 111 may be solid state LiCoO₂ (or derivative) powder and the electronic conductivity enhancer 113 can be graphitic carbon. Polymeric binder 114, such as PVDF, binds the previous two solid state
20 phases to the Al foil substrate 130. A non-aqueous liquid electrolyte 112, which is an organic solvent with dissolved lithium salt, is soaked into the pores of the composite cathode 110. Liquid electrolyte 112 has a high lithium ion conductivity of 10⁻² - 10⁻³ S/cm at 25°C, when 100% of the measurement volume is electrolyte. Liquid electrolyte 112 may reach almost every volume element inside the composite cathode, except for those volume elements that
25 are already taken by the electrochemically active cathode material 111, the electronic conductivity enhancer 113 and, to some extent, the polymeric binder 114. The composite cathode 110 may have an effective overall lithium ion conductivity throughout its bulk of approximately 10⁻³ - 10⁻⁴ S/cm at 25°C given that the electrolyte 112 can be present in, for example, only about 30% of the composite cathode volume and additionally may, for
30 example, have torturous pathways to overcome in the pores to unfold its lithium conductivity.

[0065] Further shown in Figure 1 are the non-aqueous liquid electrolyte 112 soaked, perforated polymeric separator 120 (typically 13 – 50 μ m thick) and a typical Li-ion or Li-polymer anode 140. A Li-ion or Li-polymer anode 140 is typically around 100 μ m thick and

consists of electrochemical anode material 141, usually provided through graphitic carbon, a polymeric binder 142 that is optimized for graphitic carbon, and non-aqueous liquid electrolyte 112. Additional cell components exist, such as the Cu anode current collector foil and cell packaging, but are not included in Figure 1.

5 **[0066]** Figure 2 shows one of the exemplary embodiments of the present invention. Composite cathode 210 may be composed of, for example, at least three solid state phases (without any liquid phases present): (1) at least one solid-state electrochemically active cathode material 211 such as, for instance, LiCoO_2 ; (2) at least one solid-state electronically conducting material 213, such as, for instance, Ni, which has an electronic conductivity that
10 may be at least three times higher than the electronic conductivity of said electrochemically active cathode material 211 prior to its initial charge; and (3) at least one solid-state, inorganic, ionically conducting material 212, such as, for instance, $\text{Li}_{0.35}\text{La}_{0.55}\text{TiO}_3$, which may have an ionic conductivity that may be at least three times higher than the ionic conductivity of the electrochemically active cathode material 211 prior to its initial charge.

15 **[0067]** Composite cathode 210 of certain embodiments of the present invention may not require any pores for a liquid non-aqueous electrolyte and thus may be fabricated in a denser fashion (*e.g.*, typical residual porosity of less than 20%) and annealed at higher temperatures for improved grain boundary bonding. Composite cathode 210 of certain
20 embodiments of the present invention may be easily fabricated with increased thickness (*e.g.*, 100-1000 μm) and good mechanical properties. In certain embodiments of the present invention, composite cathode 210 may have sufficient rigidity so that it is able to serve as its own substrate or substrate for the other cell components, such as, for instance, 1.5 μm thick solid-state thin-film electrolyte 220 and thin-film metallic lithium anode 240.

25 **[0068]** Figure 3 shows another alternative preferred embodiment of the present invention. Composite cathode 310 may be composed of at least two solid state phases (without any liquid phases present): (1) at least one solid-state electrochemically active cathode material 311 such as, for instance, surface modified LiCoO_2 with strongly enhanced lithium ion grain boundary conductivity; and (2) at least one solid-state electronically
30 conducting material 313, such as, for instance Ni, which has an electronic conductivity that may be at least three times higher than the electronic conductivity of said electrochemically active cathode material 311 prior to its initial charge. The provision of surface modified LiCoO_2 with strongly enhanced lithium ion grain boundary conductivity may make obsolete

the need for a separate, solid-state, inorganic, ionically conducting material, such as element 212 in Figure 2.

[0069] Composite cathode 310 of certain embodiments of the present invention may not require any pores for a liquid non-aqueous electrolyte and thus may be fabricated in a denser fashion (typical residual porosity of less than 20%) and annealed at higher temperatures for improved grain boundary bonding. Composite cathode 310 of certain embodiments of the present invention may be easily fabricated with increased thickness (*e.g.*, 100-1000 μ m) and good mechanical properties. In most cases, composite cathode 310 of certain embodiments of the present invention may have sufficient rigidity so that it is able to serve as its own substrate or substrate for the other cell components, such as, for instance, 1.5 μ m thick solid-state thin-film electrolyte 320 and thin-film metallic lithium anode 340.

[0070] The embodiments and examples described above are exemplary only. One skilled in the art may recognize variations from the embodiments specifically described here, which are intended to be within the scope of this disclosure and invention. As such, the invention is limited only by the following claims. Thus, it is intended that the present invention cover the modifications of this invention provided they come within the scope of the appended claims and their equivalents.

WHAT IS CLAIMED IS:

1. A rechargeable electrochemical device comprising:
a positive composite cathode, said positive cathode comprising:
 - a solid-state electrochemically active material comprising an electronic conductivity and an ionic conductivity in a pre-charged state of the electrochemically active material;
 - a solid-state electronically conducting material comprising an electronic conductivity that is at least three times higher than the electronic conductivity of said electrochemically active material in its pre-charged state, and
 - a solid-state, inorganic, ionically conducting material, which has an ionic conductivity that is at least three times higher than the ionic conductivity of said electrochemically active material in its pre-charged state.
2. A rechargeable electrochemical device comprising:
a positive composite cathode comprising:
 - a solid-state electrochemically active material comprising an electronic conductivity and an ionic conductivity; and
 - a solid-state, ionically conducting material, which comprises a different material than said electrochemically active material;wherein the electrochemical device does not comprise liquid and the electrochemical device does not comprise gel-like solvent.
3. The electrochemical device of claim 1 wherein said electrochemically active material provides more electronic conductivity for said positive composite cathode than any other material within said positive composite cathode.
4. The electrochemical device of claim 2 wherein said electrochemically active material provides more electronic conductivity for said positive composite cathode than any other material within said positive composite cathode.
5. The electrochemical device of claim 2 further comprising an electronically conducting material comprising an electronic conductivity at least three times higher

than said electronic conductivity of said electrochemically active material in its pre-charged state.

6. The electrochemical device of claim 2 wherein said ionically conducting material has an ionic conductivity at least three times higher than said ionic conductivity of said electrochemically active material .

7. The electrochemical device of claim 2 wherein said ionically conducting material is the same material as said electrochemically active material.

8. The electrochemical device of claim 2, further comprising a solid state electrolyte, which does not comprise a liquid and which does not comprise a gel-like solvent.

9. A rechargeable electrochemical device comprising:
a solid state positive cathode,
a negative anode, and
a solid state electrolyte sandwiched between said cathode and said anode;
wherein said electrochemical device has a rated capacity of at least 2 mAh/cm² based on the geometric footprint of said positive cathode.

10. The electrochemical device of claim 9 wherein said cathode comprises only solid-state electrochemically active phases.

11. The electrochemical device of claim 9 wherein said electrochemical device has a rated capacity of at least 4 mAh/cm² based on the geometric footprint of said positive cathode.

12. The electrochemical device of claim 9 wherein said electrochemical device comprises a rated capacity of at least 5 mAh/cm² based on the geometric footprint of said positive cathode.

13. The electrochemical device of claim 9 wherein said electrochemical device comprises a rated capacity of at least 17 mAh/cm² based on the geometric footprint of said positive cathode.

14. The electrochemical device of claim 9 wherein said electrochemical device is

fully dischargeable in less than 30 hours within its reversibility range.

15. The electrochemical device of claim 9 wherein said electrochemical device is fully dischargeable in less than 10 hours within its reversibility range.

16. The electrochemical device of claim 10 wherein said electrochemical device is fully dischargeable in less than 30 hours within its reversibility range.

17. The electrochemical device of claim 10 wherein said electrochemical device is fully dischargeable in less than 10 hours within its reversibility range.

18. The electrochemical device of claim 11 wherein said electrochemical device is fully dischargeable in less than 30 hours within its reversibility range.

19. The electrochemical device of claim 11 wherein said electrochemical device is fully dischargeable in less than 10 hours within its reversibility range.

20. The electrochemical device of claim 12 wherein said electrochemical device is fully dischargeable in less than 30 hours within its reversibility range.

21. The electrochemical device of claim 12 wherein said electrochemical device is fully dischargeable in less than 10 hours within its reversibility range.

22. The electrochemical device of claim 13 wherein said electrochemical device is fully dischargeable in less than 30 hours within its reversibility range.

23. The electrochemical device of claim 13 wherein said electrochemical device is fully dischargeable in less than 10 hours within its reversibility range.

24. The electrochemical device of claim 9 comprising a volumetric capacity density of at least 60 Ah/liter in a fully packaged state.

25. The electrochemical device of claim 9 comprising a volumetric energy density of at least 240 Wh/liter in a fully packaged state.

26. The electrochemical device of claim 10 comprising a volumetric capacity density of at least 90 Ah/liter in a fully packaged state.

27. The electrochemical device of claim 10 comprising a volumetric energy density of at least 360 Wh/liter in a fully packaged state.

28. The electrochemical device of claim 11 comprising a volumetric capacity density of at least 100 Ah/liter in a fully packaged state.

29. The electrochemical device of claim 11 comprising a volumetric energy density of at least 400 Wh/liter in a fully packaged state.

30. The electrochemical device of claim 13 comprising a volumetric capacity density of at least 250 Ah/liter in a fully packaged state.

31. The electrochemical device of claim 13 comprising a volumetric energy density of at least 1000 Wh/liter in a fully packaged state.

32. The electrochemical device of claim 9 wherein said positive cathode comprises a composite prior to its initial charge.

33. The electrochemical device of claim 9 wherein said positive cathode comprises a single phase prior to its initial charge.

34. The electrochemical device of claim 9, further comprising at least two solid state positive cathodes;

at least two negative anodes; and

at least two solid state electrolytes, each of said electrolytes sandwiched between one of said positive cathodes and one of said negative anodes;

wherein said electrochemical device comprises a rated capacity of at least 4 mAh/cm² based on the geometric footprint of said at least two positive cathodes.

35. The electrochemical device of claim 34 wherein said at least two positive cathodes comprise a smaller positive cathode and a larger positive cathode and wherein said rated capacity is based on the geometric footprint of said larger positive cathode.

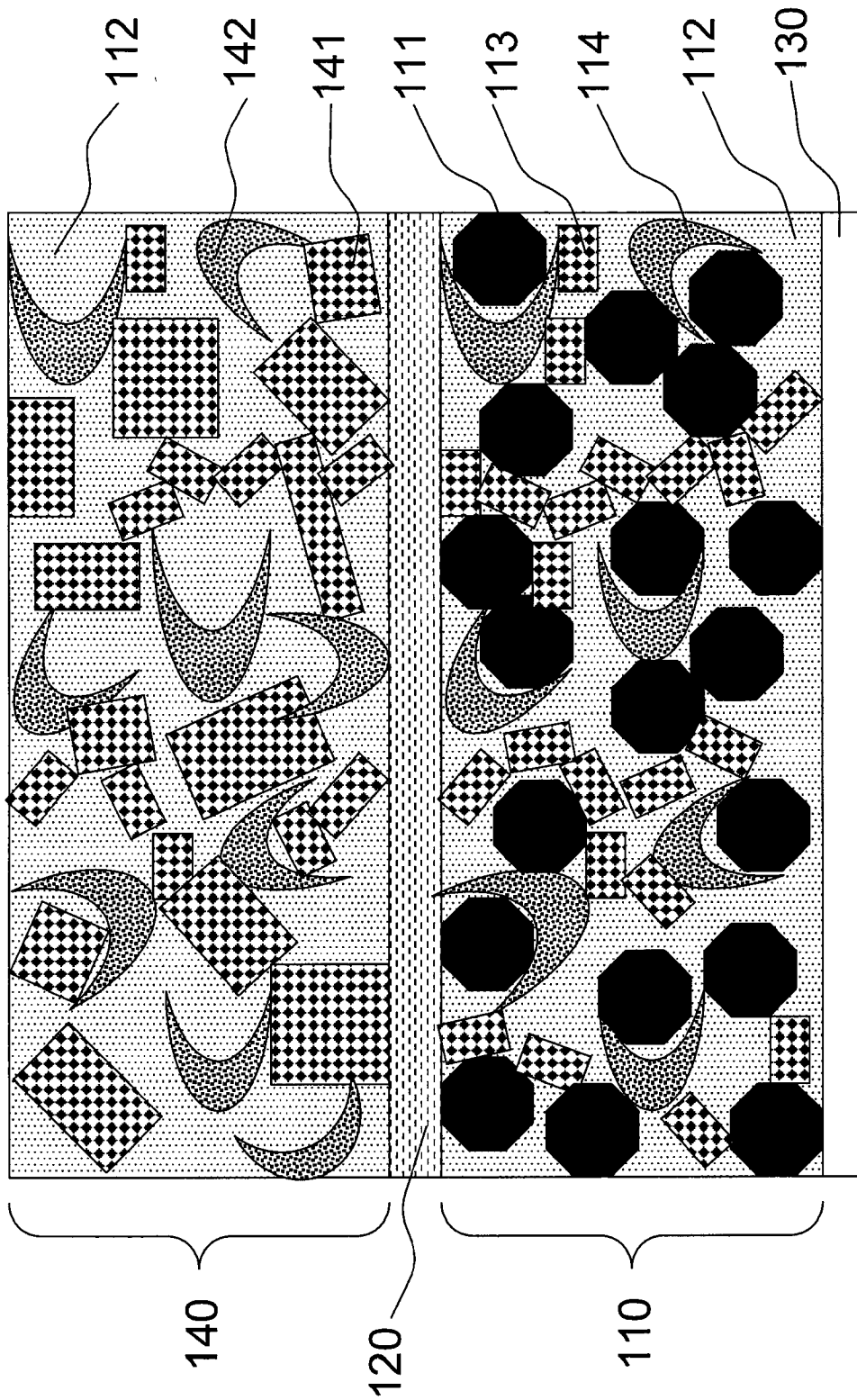


Figure 1 – Prior Art

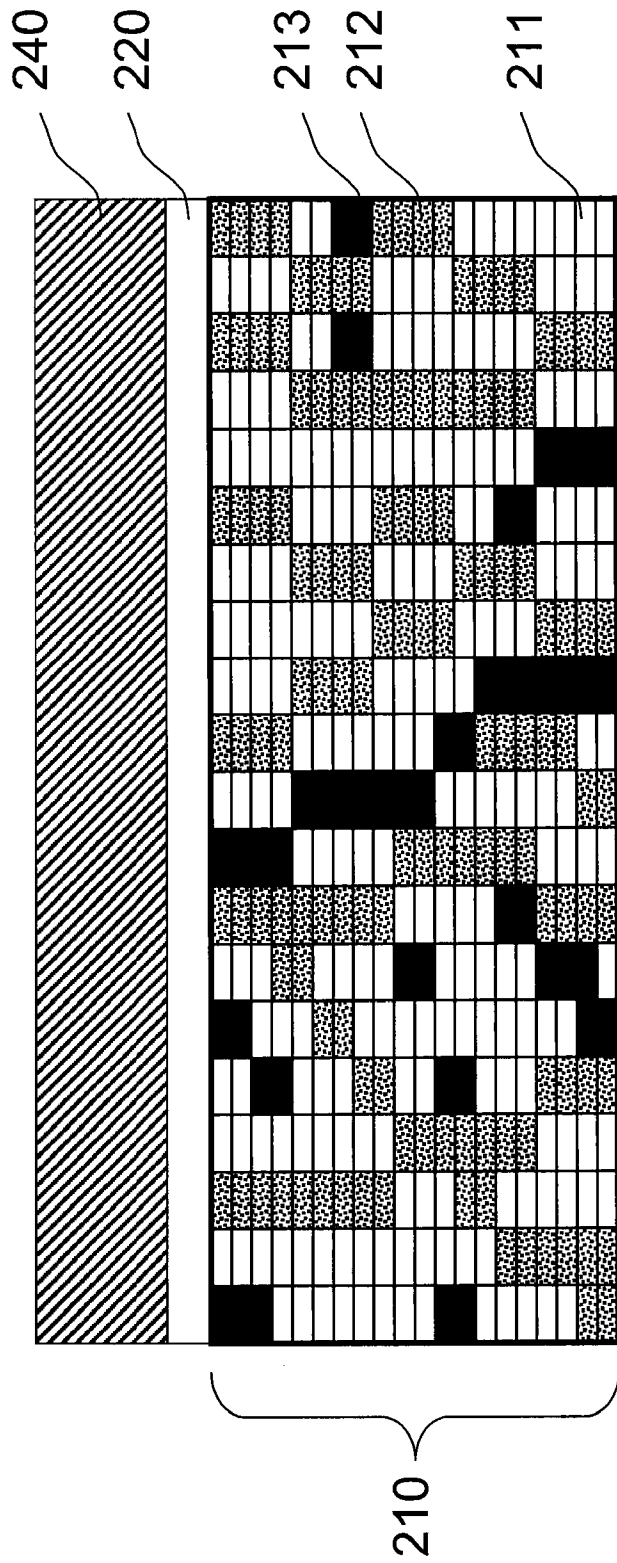


Figure 2

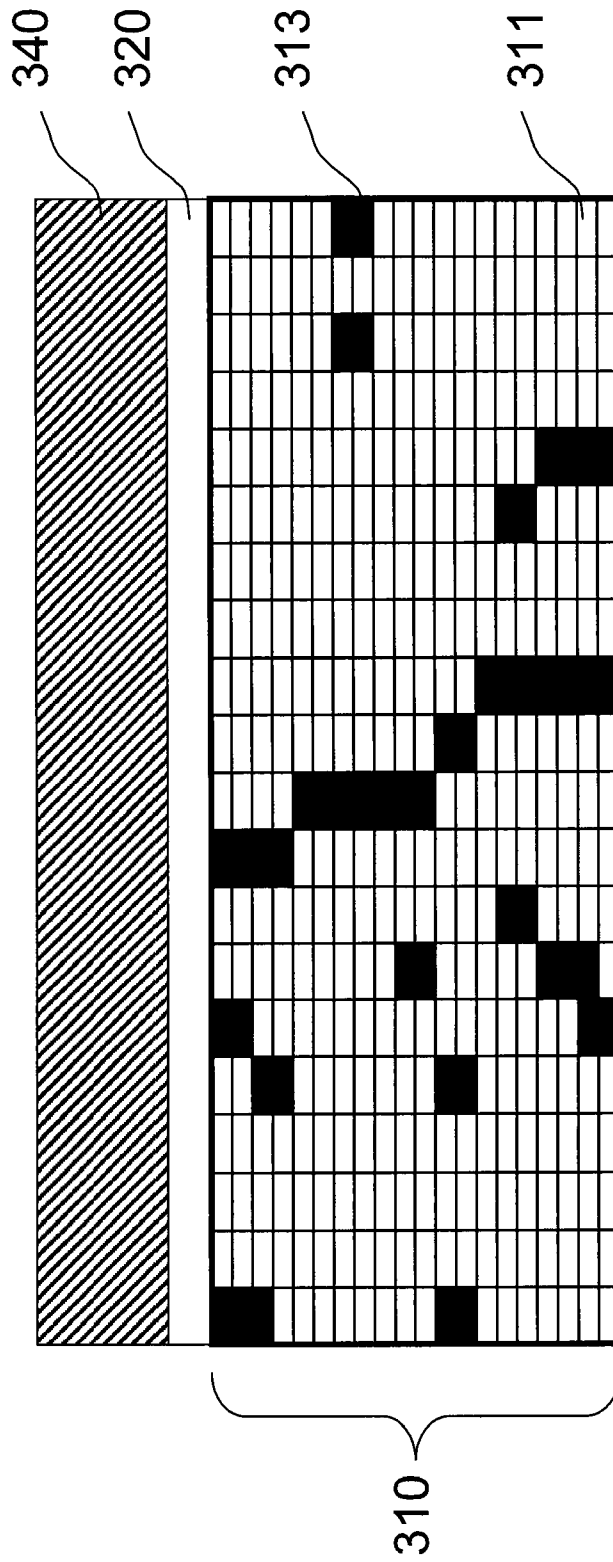


Figure 3

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2011/039467

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - H01M 4/02 (2011.01)

USPC - 429/218.1

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)

IPC(8) - H01M 4/02, 4/136, 4/36 (2011.01)

USPC - 429/218.1, 231.9, 232

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

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

Patbase, Google Patents, Google Scholar

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2009/0092903 A1 (JOHNSON et al) 09 April 2009 (09.04.2009) entire document	1, 3
Y	INAGUMA et al. High Ionic Conductivity In Lithium Lanthanum Titanate. Solid State Communications. Vol. 86 (10), pages 689-693, 1993. [retrieved on 2011-10-21] Retrieved from the Internet: <URL: http://www.sciencedirect.com/science/article/pii/S003810989390841A>. entire document	1, 3
Y	WOLFENSTINE et al. Electrical conductivity and charge compensation in Ta doped Li4Ti5O12. Vol. 180 (1), pages 582-585, 2008. [retrieved on 2011-10-21] Retrieved from the Internet: <URL: http://www.sciencedirect.com/science/article/pii/S0378775308003650>. entire document	1, 3
Y	GUY et al. Novel architecture of composite electrode for optimization of lithium battery performance. Journal of Power Sources . Vol. 157(1), pages 438-442, 2006. [retrieved on 2011-10-21] Retrieved from the Internet: <URL: http://www.sciencedirect.com/science/article/pii/S0378775305009043>. entire document	1, 3
A	US 5,302,474 A (SHACKLE) 12 April 1994 (12.04.1994) abstract, claim 1; column 6 lines 37-61; column 7 lines 36-39	1, 3

 Further documents are listed in the continuation of Box C.

* 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

21 October 2011

Date of mailing of the international search report

27 OCT 2011

Name and mailing address of the ISA/US

Mail Stop PCT, Attn: ISA/US, Commissioner for Patents

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PCT OSP: 571-272-7774

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US2011/039467

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.:
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:
See extra sheet

- 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.:
1, 3

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.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US2011/039467

This application contains the following inventions or groups of inventions which are not so linked as to form a single general inventive concept under PCT Rule 13.1. In order for all inventions to be examined, the appropriate additional examination fees must be paid.

Group I, claims 1 and 3, drawn to a rechargeable electrochemical device comprising an inorganic material.

Group II, claims 2, 4-8, drawn to a rechargeable electrochemical device that does not comprise liquid and a gel-like solvent.

Group III, claims 9-35, drawn to a rechargeable electrochemical device comprising a solid state positive cathode, a solid state electrolyte, and wherein said electrochemical device has a rated capacity of at least 2 mAh/cm² based on the geometric footprint of said positive cathode.

The inventions listed as Groups I, II and III do not relate to a single general inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons: the special technical feature of the Group I invention: an inorganic material, as claimed therein is not present in the invention of Groups II and III. The special technical feature of the Group II invention: the electrochemical device that does not comprise liquid and a gel-like solvent as claimed therein is not present in the invention of Groups I or III. The special technical feature of the Group III invention: a solid state positive cathode, a solid state electrolyte, and wherein said electrochemical device has a rated capacity of at least 2 mAh/cm² based on the geometric footprint of said positive cathode as claimed therein is not present in the invention of Groups I or II.

Groups I, II and III lack unity of invention because even though the inventions of these groups require the technical feature of a rechargeable electrochemical device, comprising a solid state positive cathode, this technical feature is not a special technical feature as it does not make a contribution over the prior art in view of US 5,302,474 A (SHACKLE) 12 April 1994 (12.04.1994) abstract, claim 1; column 6 lines 37-61; column 7 lines 36-39.

Groups I and II lack unity of invention because even though the inventions of these groups require the technical feature of a rechargeable electrochemical device, comprising a solid state positive composite cathode comprising, a solid-state electrochemically active material comprising an electronic conductivity and an ionic conductivity, a solid-state, ionically conducting material, which comprises a different material than said electrochemically active material, this technical feature is not a special technical feature as it does not make a contribution over the prior art in view of US 5,302,474 A (SHACKLE) 12 April 1994 (12.04.1994) abstract, claim 1; column 6 lines 37-61; column 7 lines 36-39.

Since none of the special technical features of the Group I, II or III inventions are found in more than one of the inventions, unity of invention is lacking.