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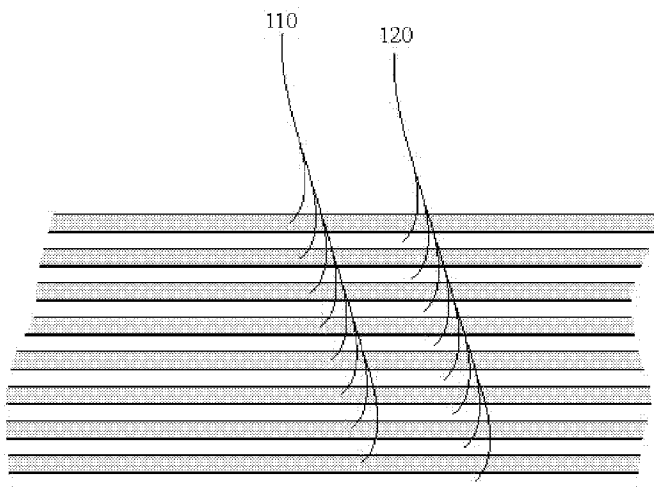


FIG. 1

(57) Abstract: An electrochemical device is claimed and disclosed, including a method of manufacturing the same, comprising an environmentally sensitive material, such as, for example, a lithium anode; and a plurality of alternating thin metallic and ceramic, blocking sub-layers. The multiple metallic and ceramic, blocking sub-layers encapsulate the environmentally sensitive material. The device may include a stress modulating layer, such as for example, a Lipon layer between the environmentally sensitive material and the encapsulation layer.



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## THIN FILM ENCAPSULATION FOR THIN FILM BATTERIES AND OTHER DEVICES

### RELATED APPLICATION(S)

5 [0001] The present application claims priority under 35 U.S.C. § 119 to U.S. provisional patent application Ser. No. 61/020,506, filed January 11, 2008, which is incorporated herein by reference in its entirety.

### FIELD OF THE INVENTION

10 [0002] The field of this invention is the device, composition, method of depositing, encapsulation and fabrication of solid-state, thin-film, secondary and primary electrochemical devices, including batteries.

### BACKGROUND OF THE INVENTION

15 [0003] Thin-film batteries (TFBs) typically may require a high-performance hermetic encapsulation that protects them against ambient chemical reactants (such as, for example, O<sub>2</sub>, H<sub>2</sub>O, N<sub>2</sub>, CO<sub>2</sub>, etc.) over many years of life time. The quality requirements for the encapsulation may be independent of the material choice of the most sensitive component in a thin-film battery, the anode (metallic lithium, lithium-ion [e.g. carbon or tin nitride], or “Li-free” anode [= current collector at which metallic lithium is plated out during TFB  
20 operation]), because any of these anodes may cease to work after a comparable amount of long-term, accumulated transmission of reactants into the TFB. For a 10-year shelf-life expectancy, for instance, the encapsulation should preferably exhibit a water vapor transmission rate (WVTR) of less than 10<sup>-3</sup> g/m<sup>2</sup>-day while the oxygen transmission rate  
25 (OTR) should preferably be smaller than 5x10<sup>-4</sup> g/m<sup>2</sup>-day. These estimated quantities are based on the complete reaction of 1.6x10<sup>-4</sup> g/cm<sup>2</sup> of lithium metal or lithium ions in the anode to either LiOH or Li<sub>2</sub>O. Furthermore, these estimated quantities represent practical rates and include reactants ingress (transmission) along the encapsulation-TFB seal area, in addition to the typical transmission rates that are measured only vertically through the encapsulation by  
30 the MOCON method.

[0004] However, current non-thin-film encapsulation is generally responsible for nearly 50% or more of the overall thickness of standard TFBs. When adjoining TFBs into a battery stack for applications for which the supply of a maximum of energy within a given

thickness is critical, one can not afford to waste 50% of the stack volume on non-energy providing encapsulation.

[0005] Thus, a need exists for the encapsulation thickness to be reduced to a minimum without compromising the protection performance.

5

### SUMMARY OF THE INVENTION

[0006] The invention pertains to, for example, a high-performance thin-film encapsulation for devices such as thin-film batteries that allows for the encapsulated devices to be fabricated much thinner than before while substantially increasing their high-  
10 temperature stability. The described approach is based on a multilayer thin-film encapsulation whose constituent sub-units comprise, for example, alternating metal getter/metal nitride diffusion blocker sub-layers, which are substantially impenetrable by oxygen and moisture.

[0007] In one embodiment, the encapsulated device is a thin-film battery with a  
15 cathode of a thickness that is greater than about  $0.5\mu\text{m}$  and less than about  $200\mu\text{m}$ . The electrolyte may be less than, for example, about  $5\mu\text{m}$  thick. The anode may be greater than, for example, about  $0.1\mu\text{m}$  and less than  $30\mu\text{m}$  thick. Also, the encapsulating layer may have alternating metal sub-layers and ceramic, blocking sub-layers which may each be at least about 500 angstroms thick. Furthermore, the alternating metal and ceramic blocking sub-  
20 layers may, for instance, comprise at least two blocking sub-layers and two metal sub-layers. Finally, in at least one embodiment, the total thickness of every metal sub-layer and every ceramic blocking sub-layer combined may be less than about  $5\mu\text{m}$ .

[0008] In another embodiment, the encapsulated device is a battery and employs the battery-type and thin-film encapsulation described in the previous paragraph and stacks a  
25 plurality of cells. A total thickness for a five-cell stack may preferably be generally less than about 0.5mm.

### BRIEF DESCRIPTION OF FIGURE

[0009] FIG. 1 shows a section of a multilayer thin film used to encapsulate an  
30 electrochemical device according to an embodiment of the present invention.

### DETAILED DESCRIPTION

[0010] FIG. 1 shows a section of a multilayered thin film used to encapsulate an electrochemical device according to one embodiment of the present invention. The thin encapsulation material may comprise, for example, multiple strong metallic getter sub-layers 110 with alternating amorphous or glassy oxide or nitride ceramic blocking sub-layers 120. The strong metallic getter sub-layers 110 may be used, for example, to protect the device from moisture and oxygen. The strong metallic sub-layers may, for example, be comprised of Zr, Y, Ti, Cr, Al, or any alloy thereof. The amorphous or glassy ceramic blocking sub-layers 120 may be oxides, nitrides, carbides, silicides, or borides of the metal or metals used in the getter sub-layers, such as, for example, ZrO<sub>2</sub>, ZrN, ZrC, ZrB<sub>2</sub>, ZrSi, Y<sub>2</sub>O<sub>3</sub>, YN, YC, YB<sub>6</sub>, YSi, TiO<sub>2</sub>, TiN, TiC, TiB<sub>2</sub>, TiSi, Cr<sub>2</sub>O<sub>3</sub>, CrN, Cr<sub>3</sub>C<sub>2</sub>, CrB<sub>2</sub>, CrSi, Al<sub>2</sub>O<sub>3</sub>, AlN, Al<sub>4</sub>C<sub>3</sub>, AlB<sub>2</sub>, Al<sub>4</sub>Si<sub>3</sub>, or any multi-element compound thereof. The amorphous or glassy sub-layers of these rather covalently bonded materials are typically densely packed arrangements of the constituent atoms while allowing very limited or no diffusion of moisture or oxygen through their bulk. As a result, this multilayered thin film may effectively block, for example, any moisture or oxygen diffusion through its bulk and along its interfaces and may also protect the underlying, air sensitive metallic anode. Furthermore, the sub-layers may have a combined thickness that is sufficient to frustrate oxygen and moisture penetration.

[0011] Among certain available materials, a layer of metal (sheet, foil, or thin films) may provide the most efficient protection against oxygen and moisture, particularly when the metal can be hermetically sealed around the environmentally-sensitive body. Specifically, for the protection of thin-film devices it would be most preferable to apply a metallic thin film encapsulation that creates a tent-like construction over a device having a substrate and attaching the encapsulation to the substrate along a surface next to the device in a tightly-sealed fashion.

[0012] The optimized encapsulation approach specifically designed for TFBs consists of a multilayer construction formed by a plurality of thin metal sub-layers with alternating amorphous or glassy inorganic oxide and/or nitride and/or carbides, and/or silicides, and/or borides sub-layers that exhibit little or no grain structure. In particular, certain "grainless" nitrides, carbides, silicides, and borides possess very dense material morphologies that effectively block the diffusion paths for any oxygen and/or moisture that may have penetrated the neighboring thin metal sub-layers.

[0013] In an embodiment in the present invention, metals may be chosen from well known O<sub>2</sub> and/or H<sub>2</sub>O getters, such as Zr, Y, Ti, Cr, Al, and/or alloys thereof. The diffusion blocking, inorganic amorphous or glassy sub-layers may be selected from materials such as ZrO<sub>2</sub>, ZrN, Y<sub>2</sub>O<sub>3</sub>, YN, Cr<sub>2</sub>O<sub>3</sub>, CrN, Al<sub>2</sub>O<sub>3</sub>, AlN, and/or multinary compound compositions and derivatives thereof, such as TiAlN<sub>x</sub>O<sub>y</sub>.

[0014] These thin-film encapsulation sub-layers can be deposited by, for example, metal sputtering with alternating compound deposition using one single sputter cathode in one vacuum deposition chamber without sample change. This may be performed by simply switching back and forth between Ar and Ar-N<sub>2</sub>-O<sub>2</sub> sputtering of the same metal (e.g., TiAl). The result may be a 3μm thick, 30-layer construction of 0.1μm TiAl / 0.1μm TiAlN<sub>x</sub>O<sub>y</sub> / 0.1μm TiAl / 0.1μm TiAlN<sub>x</sub>O<sub>y</sub> / ..., which may be difficult for O<sub>2</sub> and H<sub>2</sub>O to penetrate or permeate in vertical direction. To avoid compromising this high-performance encapsulation through seal leaks at the encapsulation-substrate interface (seal area), specific attention may be given to the substantially defect-free deposition of these layers in the seal area. This objective may be accomplished through an appropriately prepared substrate surface and a substantially flawless thin-film layer deposition.

[0015] This type of multilayer thin-film encapsulation embodiment may not only preferably be about 3μm thin (reduces the thickness of the TFB from 150μm to about 80μm) but may also be as substantially flexible as any of the other battery component layers, such as the 3μm LiCoO<sub>2</sub> cathode. Fine-tuning of the flexibility of the multilayer thin-film encapsulation may be achieved through a change in physical vapor deposition (PVD) parameters and/or change in materials selection, such as resorting to Zr / ZrN / Zr / Zr<sub>2</sub>N / Zr / Zr<sub>x</sub>N / Zr ... instead of TiAl / TiAlN<sub>x</sub>O<sub>y</sub> / TiAl / ....

[0016] A metallic lithium anode is chemically stable with, for instance, Zr and/or ZrN. However, the metallic lithium anode can be soft and, as it is known of most anode materials today, may be susceptible to substantial expansion and contraction during TFB operation. Mechanical features such as these can be challenging for the multilayer thin-film encapsulation, potentially causing cracks due to stress imbalance at the lithium anode/encapsulation interface. Once the encapsulation is cracked, the underlying lithium anode may be exposed to air and thus may chemically deteriorate.

[0017] To counteract this stress imbalance, a stress modulating layer, such as a thin-film layer of Lipon, may be introduced between the metallic lithium anode and the multilayer thin-film encapsulation. Lipon has been proven to be chemically and mechanically stable

with TiAl, TiAlN<sub>x</sub>O<sub>y</sub>, Zr, ZrN, etc., as well as with lithium alloys, lithium solid solutions, and metallic lithium. The Lipon electrolyte layer that is located underneath the metallic lithium anode, together with the overlying Lipon stress modulation layer, can confine the interposed metallic lithium anode while protecting it, not only mechanically but also chemically, as  
5 Lipon is compatible with metallic lithium. In this configuration where the metallic lithium anode is confined within the layers of Lipon, it may remain fixed within its location and electrochemically intact even when heated above its melting point of 181°C.

This engineering design of some embodiments utilizing this configuration may enable the TFB to be used in solder reflow or flip chip processing. Aided through this design, the  
10 multilayer thin-film encapsulation does not only provide the TFB with much less thickness but also with a much higher temperature stability (>150°C continuous) than the surlyn/metal foil encapsulation currently used in industry.

[0018] In other embodiments, alloys or solid solutions of lithium (e.g. Li<sub>x</sub>Cu, Li<sub>x</sub>Zr, Li<sub>x</sub>V, Li<sub>x</sub>W), which electrochemically behave very similar to a metallic lithium anode, may  
15 be used as the anode, offering stronger mechanical properties compared to the soft lithium anode, thereby allowing the direct deposition of the multilayer thin-film encapsulation without the use of the Lipon stress modulation layer. The resulting multilayer thin-film encapsulation may still allow the TFB to maintain a high temperature stability (>150°C continuous), just as the one configured with the Lipon stress modulation layer.

[0019] Once the multilayer thin-film encapsulation in certain embodiments is  
20 demonstrated to be chemically and mechanically stable with the metallic lithium anode, or lithium alloy, under TFB operation, the present invention in certain embodiments may deposition-pattern the multilayer thin-film encapsulation in a fashion that renders it selectively conducting and insulating in other areas. This way, the multilayer thin-film  
25 encapsulation can also serve as the anode current collector, or negative terminal, without short-circuiting the TFB through the metallic substrate, which is configured as the positive terminal in IPS' TFBs fabricated on metal foil.

### EXAMPLES OF EMBODIMENTS

[0020] Example 1: Some embodiments use the encapsulation method described to  
30 protect a lithium anode from moisture and air. These embodiments comprise a 1 in<sup>2</sup> metal foil substrate measuring approximately 50µm in thickness. A 0.5µm thick conductive barrier layer is disposed on at least one surface of the substrate using one of the methods generally

available to one ordinarily skilled in the art in addition to those described here. A 3.5 $\mu\text{m}$  thick LiCoO<sub>2</sub> positive cathode is disposed onto the conductive barrier layer. A 1.2 $\mu\text{m}$  thick Lipon electrolyte layer is disposed onto the cathode layer and a 9 $\mu\text{m}$  thick Li anode is disposed onto the electrolyte. A 3 $\mu\text{m}$  thick thin-film multilayer encapsulation, consisting of 5 15 sub-layers of 0.1 $\mu\text{m}$  Zr alternated with 15 sub-layers of 0.1 $\mu\text{m}$  of ZrN, is then disposed on the layered device. This specific embodiment can achieve 500h in 85°C/85%RH environment.

[0021] Example 2: Other embodiments may combine five of the encapsulated battery cells discussed previously. This embodiment generally has a total thickness less than 0.5mm and supplies 2.5mAh at 1/2C rate at 25°C between 4.2 – 2.0V. 10

[0022] Example 3: Yet other embodiments of the present invention comprise a 0.5 $\mu\text{m}$  conductive barrier layer, a LiCoO<sub>2</sub> positive cathode with a thickness of about 12 $\mu\text{m}$ , a 1.2 $\mu\text{m}$  Lipon electrolyte layer, a Li anode with a thickness of about 10 $\mu\text{m}$ , and a 2 $\mu\text{m}$  thick Lipon modulator layer on top of the Li anode. These embodiments may be fabricated on a 50 $\mu\text{m}$  metal foil substrate of 1 in<sup>2</sup> in area and encapsulated by a 3 $\mu\text{m}$  thin-film encapsulation. This 15 embodiment has a total thickness of less than 80 $\mu\text{m}$  and generally supplies 2mAh at 1/2C rate at 25°C between 4.2 – 2.0V.

[0023] Example 4: Further, other embodiments of the present invention may comprise the electrochemical device from Example 1. Due to the high-melting point of Zr-ZrN 20 (>>1000°C), the encapsulation is capable of withstanding temperatures of up to 265°C—the maximum temperature encountered in lead-free solder reflow processing—for extended periods of time. This chemical and physical stability of the electrochemical device is achieved despite the melting of the metallic lithium anode that does, however, not react with Zr or ZrN under these conditions.

[0024] Example 5: Yet, other embodiments of the present invention comprise a 25 selectively conductive encapsulation wherein, through thin-film deposition patterning such as may be accomplished by shadow-masking, certain areas of the encapsulation are made electrically conductive while some others are fabricated electrically insulating. The electrically conductive areas comprise metallic sub-layers and/or electrically conductive 30 ceramic sub-layers while the electrically insulating areas comprise ceramic non-conducting sub-layers, such as, for instance ZrO<sub>2</sub>. The selectively conductive encapsulation allows it to be used as an electrical terminal of the electrochemical device.

[0025] 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 and 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.

[0026] 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, although any methods, techniques, devices, or materials similar or equivalent to those described herein 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.

[0027] All patents and other publications identified are incorporated herein by reference for the purpose of describing and disclosing, for example, the methodologies described in such publications that might be used 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.

[0028] The embodiments 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. 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. Further, specific explanations or theories regarding the formation or performance of electrochemical devices according to the present invention are presented for  
5 explanation only and are not to be considered limiting with respect to the scope of the present disclosure or the claims.

What is claimed is:

1. An electrochemical device comprising:  
an environmentally sensitive layer; and  
a thin encapsulation layer deposited over said sensitive layer, comprising a plurality of alternating metallic sub-layers and ceramic sub-layers.
2. The electrochemical device of claim 1 wherein said metallic sub-layers comprise at least one element selected from the group comprising: scandium, yttrium, lanthanum, titanium, zirconium, hafnium, vanadium, niobium, tantalum, chromium, molybdenum, tungsten, manganese, iron, cobalt, nickel, copper, zinc, boron, aluminum, carbon, silicon, germanium, beryllium, magnesium, calcium, strontium, barium, lithium, sodium, potassium, rubidium, and caesium.
3. The electrochemical device of claim 1 wherein said ceramic sub-layers comprise nitrides of at least one element selected from the group comprising: scandium, yttrium, lanthanum, titanium, zirconium, hafnium, vanadium, niobium, tantalum, chromium, molybdenum, tungsten, manganese, iron, cobalt, nickel, copper, zinc, boron, aluminum, carbon, silicon, germanium, beryllium, magnesium, calcium, strontium, barium, lithium, sodium, potassium, rubidium, and caesium.
4. The electrochemical device of claim 1 wherein said ceramic sub-layers comprise oxides of at least one element selected from the group comprising: scandium, yttrium, lanthanum, titanium, zirconium, hafnium, vanadium, niobium, tantalum, chromium, molybdenum, tungsten, manganese, iron, cobalt, nickel, copper, zinc, boron, aluminum, carbon, silicon, germanium, beryllium, magnesium, calcium, strontium, barium, lithium, sodium, potassium, rubidium, and caesium.
5. The electrochemical device of claim 1 wherein said ceramic sub-layers comprise carbides of at least one element selected from the group comprising: scandium, yttrium, lanthanum, titanium, zirconium, hafnium, vanadium, niobium, tantalum, chromium, molybdenum, tungsten, manganese, iron, cobalt, nickel, copper, zinc, boron, aluminum, silicon, germanium, beryllium, magnesium, calcium, strontium, barium, lithium, sodium, potassium, rubidium, and caesium.
6. The electrochemical device of claim 1 wherein said ceramic sub-layers comprise silicides of at least one element selected from the group comprising: scandium,

yttrium, lanthanum, titanium, zirconium, hafnium, vanadium, niobium, tantalum, chromium, molybdenum, tungsten, manganese, iron, cobalt, nickel, copper, zinc, boron, aluminum, carbon, germanium, beryllium, magnesium, calcium, strontium, barium, lithium, sodium, potassium, rubidium, and caesium.

7. The electrochemical device of claim 1 wherein said ceramic sub-layers comprise borides of at least one element selected from the group comprising: scandium, yttrium, lanthanum, titanium, zirconium, hafnium, vanadium, niobium, tantalum, chromium, molybdenum, tungsten, manganese, iron, cobalt, nickel, copper, zinc, aluminum, carbon, silicon, germanium, beryllium, magnesium, calcium, strontium, barium, lithium, sodium, potassium, rubidium, and caesium.

8. The electrochemical device of claim 1 wherein said environmentally sensitive layer comprises at least one material selected from the group consisting of: lithium alloy, lithium solid solution, metallic lithium, titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, zinc,, zirconium, niobium, molybdenum, palladium, silver, hafnium, tantalum, tungsten, iridium, platinum, gold, beryllium, magnesium, calcium, strontium, barium, boron, aluminum, indium, carbon, silicon, germanium, tin, lead, phosphorus, arsenic, antimony, and bismuth.

9. The electrochemical device of claim 1 further comprising a stress modulation layer disposed between said environmentally sensitive layer and said encapsulation layer.

10. The electrochemical device of claim 9 wherein said stress modulation layer is not reactive with either said environmentally sensitive layer or said thin encapsulation layer.

11. The electrochemical device of claim 9 where said stress modulation layer comprises Lipon.

12. The electrochemical device of claim 1 where said environmentally sensitive layer is soft.

13. The electrochemical device of claim 12 wherein said soft, environmentally sensitive layer comprises of at least one material selected from the group consisting of: lithium alloy, lithium solid solution, and metallic lithium.

14. The electrochemical device of claim 1 wherein at least one sub-layer of said encapsulation layer is deposited using sputtering from a metallic target.

15. The electrochemical device of claim 1 wherein at least one sub-layer of said encapsulation layer is deposited using a dual sputter cathode deposition method.
16. The electrochemical device of claim 1 wherein said environmentally sensitive material comprises an anode.
17. The electrochemical device of claim 1 wherein said device maintains thermal stability under solder reflow conditions of up to 265°C.
18. The electrochemical device of claim 1 wherein said encapsulating layer is selectively conductive.
19. The electrochemical device of claim 18 wherein said selectively conductive thin encapsulation serves as one electrical terminal of said device.
20. The electrochemical device of claim 1 wherein said encapsulation layer is flexible.
21. The electrochemical device of claim 1 further comprising:
  - a cathode;
  - an electrolyte deposited on said cathode;
  - an anode deposited on said electrolyte;
  - a stress modulating layer deposited between said anode and said encapsulation layer.
22. The electrochemical device of claim 21 wherein said cathode comprises  $\text{LiCoO}_2$ .
23. The electrochemical device of claim 21 wherein said electrolyte comprises Lipon.
24. The electrochemical device of claim 21 wherein said anode comprises at least one material selected from the group consisting of: lithium alloy, lithium solid solution, and metallic lithium.
25. The electrochemical device of claim 21 wherein said stress modulating material comprises Lipon.
26. The electrochemical device of claim 21 wherein said cathode thickness is between about 0.5 $\mu\text{m}$  and 200 $\mu\text{m}$ .

27. The electrochemical device of claim 21 wherein said electrolyte thickness is less than about 5 $\mu$ m.

28. The electrochemical device of claim 21 wherein said anode thickness is between about 0.1 $\mu$ m and 30 $\mu$ m.

29. The electrochemical device of claim 21 wherein the thickness of said alternating metallic layers and ceramic layers are each at least about 500 angstroms.

30. The electrochemical device of claim 1 wherein said alternating metallic and blocking layers comprise at least two metallic sub-layers and at least two ceramic sub-layers, respectively.

31. The electrochemical device of claim 30 wherein the total thickness of every metallic layer and every ceramic layer is less than about 5 $\mu$ m.

32. An electrochemical device comprising:  
a cathode;  
an electrolyte deposited on said cathode;  
a soft, environmentally sensitive anode deposited on said electrolyte;  
a stress modulating layer deposited on said anode;  
an encapsulation layer, comprising a plurality of alternating metallic and ceramic sub-layers, deposited on said modulating layer.

33. An electrochemical device comprising:  
a LiCoO<sub>2</sub> layer;  
a first Lipon layer deposited on said LiCoO<sub>2</sub> layer;  
a lithium layer deposited on said first Lipon layer;  
a second Lipon layer deposited on said lithium layer; and  
an encapsulation layer, comprising a plurality of alternating metallic and ceramic sub-layers, deposited on said second Lipon layer.

34. An electrochemical device comprising:  
a cathode greater than about 0.5 $\mu$ m and less than about 200 $\mu$ m thick;  
an electrolyte less than about 5 $\mu$ m thick;  
an anode greater than about 0.1 $\mu$ m and less than about 30 $\mu$ m thick;  
a modulating layer; and

a plurality of alternating metallic and ceramic sub-layers, wherein each sub-layer is less than about 5 $\mu$ m thick.

35. A method of manufacturing an electrochemical device comprising:  
depositing an environmentally sensitive layer; and  
depositing a plurality of alternating metallic sub-layers and ceramic sub-layers.

36. The method of claim 35 wherein said environmentally sensitive layer comprises at least one material selected from the group consisting of: lithium alloy, lithium solid solution, and metallic lithium.

37. The method of claim 35 further comprising a stress modulator layer deposited over said sensitive layer.

38. The method of claim 35 where said environmentally sensitive layer is soft.

39. The method of claim 38 wherein said soft, environmentally sensitive layer comprises at least one material selected from the group consisting of: lithium alloy, lithium solid solution, and metallic lithium.

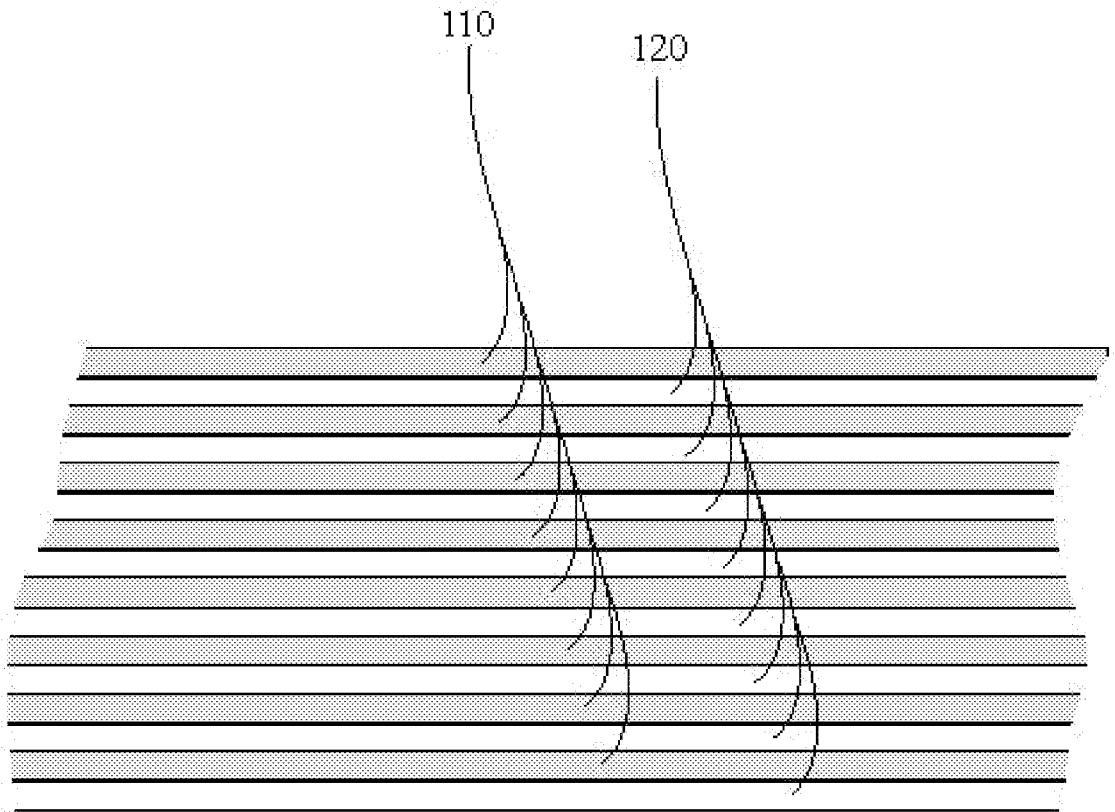
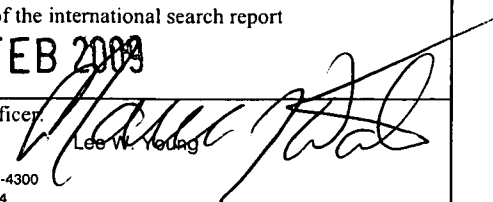


FIG. 1

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 09/30551

<b>A. CLASSIFICATION OF SUBJECT MATTER</b> IPC(8) - H01M 10/04, H01M 4/02, H01M 2/02 (2009.01) USPC - 29/623.5, 429/162, 429/185, 29/623.1 According to International Patent Classification (IPC) or to both national classification and IPC		
<b>B. FIELDS SEARCHED</b> Minimum documentation searched (classification system followed by classification symbols) IPC(8) - H01M 10/04, H01M 4/02, H01M 2/02 (2009.01) USPC - 29/623.5, 429/162, 429/185, 29/623.1 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched USPC - 29/623.5, 429/162, 429/185, 29/623.1 IPC(8) - H01M 10/04, H01M 4/02, H01M 2/02 (2009.01) (text delimited) Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) Google, Google Patent, PubWEST Electrochemical, environmentally sensitive layer, encapsulation, lithium, Lipon, anode, cathode, electrolyte, metallic, ceramic, oxide, nitride, carbide, boride, silicide		
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X --- Y	US 2007/0264564 A1 (Johnson et al.) 15 November 2007 (15.11.2007), entire document, especially para [0003], [0031], [0035], [0037], [0052]	1-3, 8, 16, 20, 30 ----- 4-7, 9-15, 17-19, 21-29, 31-33, 35-39
X --- Y	US 2007/0184345 A1 (Neudecker et al.) 09 August 2007 (09.08.2007), entire document, especially para [0014], [0019], [0049], [0050], [0080]-[0085], [0090], [0091]	34 ----- 9-15, 17-19, 21-29, 31-33, 35-39
Y	US 2005/0072458 A1 (Goldstein) 07 April 2005 (07.04.2005), para [0082]	4-7
Y	US 2004/0048157 A1 (Neudecker et al.) 11 March 2004 (11.03.2004), para [0101]	14, 15
<input type="checkbox"/> 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 16 February 2009 (16.02.2009)		Date of mailing of the international search report <b>26 FEB 2009</b>
Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-3201		Authorized officer:  Lee W. Young PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774