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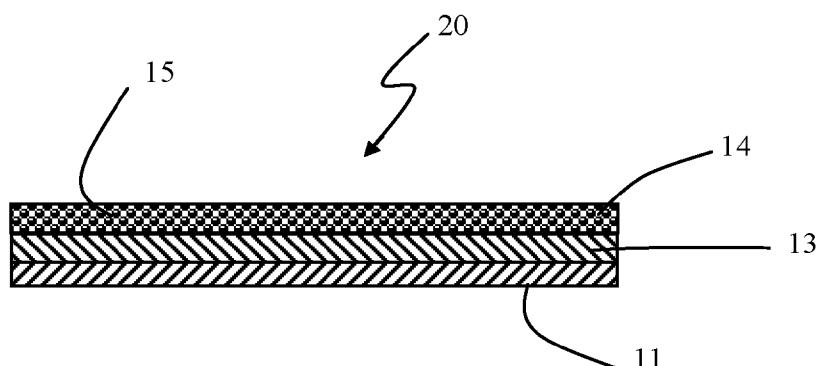
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(54) Title: IMPROVED MULTI-LAYER COMPOSITE GETTER



**Fig. 2**

(57) Abstract: An improved multi-layer composite getter is disclosed, as well as a method for its manufacturing and electrochemical devices for energy storage that employ said multi-layer getter composites.

## IMPROVED MULTI-LAYER COMPOSITE GETTER

The present invention relates to an improved multi-layer composite getter, a method for its manufacturing and to electrochemical devices for energy storage that 5 employ said multi-layer composite getters.

The use of getter materials for the removal of gaseous impurities has found application in many fields, such as process chambers for semiconductor devices, purification of process gases and pumping members for evacuated chambers. However, one of the fields in which the use of getter materials is particularly appreciated is that of 10 the removal of harmful species from the internal volume of hermetic or sealed devices, wherein the presence of these harmful species jeopardizes the operation of the device.

In this case, the mechanisms that compromise the functionality of the device are essentially of two types, the first one of which is due to a chemical interaction of the 15 harmful species with one or more components of the device, which interaction alters the properties of said components, thus jeopardizing their functionality. Examples of these interactions may be, among others, a loss of transparency for optical devices or a degradation of the electrical characteristics of the components by altering their resistivity and thus their functionality. In this first case it is very important that the concentration of harmful species, typically in the form of gases, is as low as possible.

20 A second degradation mechanism is instead associated with the risks of breaking the device due to an excessive pressurization; this problem is present in the devices in which the harmful species are mainly in a gaseous form and their production is associated with the operation of the device itself. In this case risks of mechanical breakage of the container, and thus also safety problems, are associated with a 25 malfunction of the device.

This problem is particularly felt in the field of electrochemical devices for energy storage, nowadays generally known in the field as energy storage devices.

In the wide range and variety of electrochemical devices for energy storage three 30 very important large families may be identified: rechargeable batteries, with particular reference to lithium batteries; electrolytic capacitors, with particular reference to those known in the field as "aluminum capacitors"; and "supercapacitors". In the technical

field, the main difference between the two latter categories of devices previously listed resides in the different order of magnitude of the accumulated capacity. In particular, in the case of electrolytic capacitors of small size the capacity is in the order of microfarad (μF), whereas in the case of supercapacitors the capacity may also be 10,000 times 5 higher.

The problem of the presence of gaseous impurities within these devices has been tackled in various ways. For example the published patent applications WO 2007/066372 and WO 2008/148778, both in the applicant's name, employed polymeric multi-layer systems with the getter material dispersed in a suitable polymer and shielded 10 from the contact and the interaction with the electrolyte by means of a protective polymeric layer permeable to the harmful species but impermeable to the electrolyte.

Another solution, described in patent applications WO 2007/080614 and WO 2008/148781, both in the applicant's name, teaches the use of getter materials enclosed 15 in a polymeric container permeable to the harmful species but impermeable to the electrolyte.

Finally, patent application WO 2008/033560, also in the applicant's name, exploits a completely different approach and describes the use of metal getter multi-layers for removing hydrogen from electrochemical devices for energy storage, with 20 particular reference to the use of materials comprising an external layer made of a noble metal.

The latter solution seems, and is so considered in the field, better than the previous ones with reference to the removal of H<sub>2</sub> because the use of polymeric multi-layers necessarily limits the amount of getter material that can be used and therefore, on equal volume occupied by the getter material, results in a lower capacity. Moreover, the 25 solutions according to which the getter material is enclosed in a polymeric container have proved to be inherently fragile, in particular at the junction areas of the container. In addition to these problems, there is also the fact that according to the first two solutions the presence of the polymeric layer generally slows down hydrogen sorption, whereas the multi-layer metal getter, which is described as such in the International 30 publication WO 2006/089068 in the applicant's name, has characteristics that were considered to make it compatible with the application.

In particular, although this solution is very effective in the removal of hydrogen under normal conditions of use within electrochemical devices for energy storage, it has surprisingly shown unexpected drawbacks under some particular use conditions in which the materials intended to remove hydrogen have become themselves gas sources, 5 thus leading to the device breakage.

The main condition leading to this reverse behavior in electrolytic capacitors and in particular in the aluminum capacitors is the presence of a flow of current having reversed polarity with respect to the normal operation. This situation may result from a 10 human error during the connection and installation of the device, with a significant associated safety risk due to the large amounts of gas that may be generated in a short time, or when the inner temperature of the device exceeds the nominal temperature of the capacitor, which is typically defined in the field as "rated temperature" of the device, since in this case secondary alternating currents are generated, defined in the field as "ripple currents", whose inverse component is the one which is harmful to the device. 15 More references and details can be found in various publications such as the book *Electronic Fundamentals & Applications*, published in 1970. The intensity of the phenomenon, and thus the associated gas generation, is directly proportional to temperature; in particular this starts to be significant when the temperature of the device exceeds the specified rated temperature by 5%.

20 This kind of problem has been effectively solved thanks to the teaching of the international patent application PCT/EP2010/056872, in the applicant's name, which discloses a multi-layer getter system wherein on at least one of the surfaces of the getter material a protective layer made of palladium or palladium-based composite materials is deposited, and wherein a protective polymeric layer permeable to hydrogen is provided 25 on at least 80% of the surface area of its surface or surfaces being coated with palladium or composites thereof.

It is an object of the present invention to overcome the drawbacks still present in the prior art with reference to multi-layer metal getter materials or, as in the case of the 30 teaching disclosed in PCT/EP2010/056872 to improve the characteristics of multi-layer metal getter materials, with particular but non-exclusive reference to their use in electrochemical devices for energy storage.

In a first aspect thereof the invention is a multi-layer composite getter for hydrogen removal comprising a support essentially formed of a metal getter material with two surfaces, wherein a first layer of palladium or palladium based composites is provided on at least one of said surfaces defining a coated surface, wherein a hydrogen-permeable protective polymeric layer is provided on at least 80% of the surface of the coated surface, characterized in that one or more auxiliary getter materials are dispersed in said hydrogen-permeable protective polymeric layer with a weight concentration comprised between 5 wt% and 50 wt%, calculated on the overall weight of the polymeric layer containing the auxiliary getter material.

10 The weight concentration of the auxiliary getter materials in the polymeric protective layer is preferably comprised between 15 wt% and 30 wt%.

With the wording "auxiliary getter materials" it is meant to better indicate the presence of additional getter materials with respect to the getter layer serving as a support for the multi-layer composite getter according to the present invention, whereas 15 the wording "palladium-based composite materials" indicates materials containing at least 60 wt% of palladium. Preferred palladium composites are palladium-vanadium, palladium-nickel compounds and even more preferred are palladium-copper or palladium-silver compounds. In an even more preferred embodiment the palladium composites are in the form of alloys.

20 The invention will be better described in the following with reference to the drawings, wherein:

- figure 1 shows a broken view of a multi-layer composite getter according to the present invention;

25 - figure 2 shows an alternative embodiment of the multi-layer composite getter according to the present invention;

- figure 3 shows a third embodiment of the multi-layer composite getter according to the present invention;

30 - figure 4 shows a first embodiment of an electrochemical device for energy storage comprising an improved multi-layer composite getter according to the present invention;

- figure 5 shows a second embodiment of an electrochemical device for energy

storage comprising a multi-layer composite getter according to the present invention; and

- figure 6 shows a third embodiment of an electrochemical device for energy storage comprising a multi-layer composite getter according to the present invention.

5 In the drawings the size and dimensional ratios of some components, with particular but non-exclusive reference to the thicknesses of the layers forming the multi-layer composite getter, have been altered in order not to compromise the reading of the drawings.

10 Thanks to the modification described in the present invention with respect to the disclosure of the international application PCT/EP2010/056872, due to the presence of auxiliary getter materials dispersed therein, the polymeric membrane has also an active role in the removal of gaseous species that are harmful for the operation of the device. In particular, it is very advantageous to functionalize the membrane in order to make it sorb harmful species other than hydrogen, such as e.g. H<sub>2</sub>O and CO<sub>2</sub>, thus providing the 15 multi-layer getter system with additional functions.

15 In particular, the presence of H<sub>2</sub>O is harmful in those electrochemical devices, in which the electrolyte is not made of an aqueous solution, such as supercapacitors and batteries, wherein the presence of water, even in amounts of the order of 20-50 ppm may significantly alter the electrical characteristics of the device. Another particularly 20 relevant case is that of the electrolytic capacitors, with particular reference to "aluminum capacitors", wherein the amount of water initially present in the electrolyte tends to increase during the use of the device because it is produced by degradation and ageing reactions of the electrolyte itself. Water production alters the electrical characteristics of the device. As to CO<sub>2</sub>, the harmful effects of its presence inside 25 hermetic devices such as electrochemical devices are similar to those related to the presence of hydrogen, i.e. the presence of CO<sub>2</sub> may create or contribute to create overpressure conditions inside the device, resulting in the previously discussed drawbacks and risks.

30 Figure 1 shows an improved multi-layer composite getter 10 made according to the present invention, wherein on both the available surfaces 12, 12' of the layer 11 made of metal getter a layer 13, 13' of palladium or palladium-based composite is

provided with a protective layer 14, 14' of a hydrogen-permeable polymeric material provided thereon.

The metal getter layer 11 serves as a support for the other layers and due to this aspect in some alternative embodiments it is possible that the layer of palladium or palladium-based composites and the polymeric layer thereon are not present along the whole surface of the getter layer. In this case it is important that the layer of palladium or palladium-based composites covers at least 20% of the surface area of the getter material layer.

Anyway it is of critical importance the fact that the protective polymeric layer covers at least 80% of the overall metallic surface of the multi-layer getter system, intended as a portion of the getter material surface area not covered by palladium or palladium-based composites and surface area of palladium or palladium-based composites.

It is important to remark that in this embodiment that has two coatings of palladium or palladium composites on the two possible surfaces of the support made up of the getter material 11, the surfaces being indicated by surfaces 12 and 12', the external polymeric membranes may have different characteristics. For instance, in the embodiment shown in figure 1 the membrane 14 contains powders of an auxiliary getter material 15, whereas the membrane 14' contains no auxiliary getter material.

Other alternative embodiments may be so configured that the membrane 14 contains powders of various auxiliary getter materials, and the auxiliary getter materials contained in the membranes 14 and 14' might be the same or different from each other, so as to provide the membranes with a selective behavior or to make them suitable to remove a specific harmful species.

An alternative embodiment is shown in figure 2, wherein the layer 13 made of palladium or palladium-based composites, with the polymeric material layer 14 lying thereon and having an auxiliary getter material dispersed therein, is provided on only one of the surfaces of the supporting getter layer 11. Also in this case the auxiliary getter material is shown as a discrete getter material in a particulate form. The same considerations previously described with reference to the possible reduced surface area of the layer of palladium or palladium-based composites also apply in this case. In

particular, in this embodiment it is preferred that the protective polymeric layer containing the getter material covers at least 80% of the surface area of solely the surface coated with palladium or palladium-based composites. In this case in fact the multi-layer composite getter is typically employed by arranging the non-coated surface 5 against a wall of the device, that in this way acts as a shield, thus protecting the getter material and making further coatings superfluous and not necessary on the surface contacting the wall of the hermetic /sealed device.

A further variant of this embodiment is shown in figure 3, where in this case it is explicitly shown that a small part 35 of the available metallic surface area of the getter 10 material is not coated by the polymeric layer 14, that contains an auxiliary getter material 15, also in this case shown in a discrete form as a dispersed particulate.

In the present invention it is important that the hydrogen-permeable polymeric material layer containing the auxiliary getter material coats at least 80% of the metallic surface exposed to the inner atmosphere of the device, where the multi-layer getter 15 system is installed.

Preferably the permeability to hydrogen of the protective polymeric layer is equal to or higher than  $10^{-12} \text{ cm}^3 \text{ cm cm}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$  at 25°C, 1 bar. This permeability value must not be referred to the properties of the protective polymeric layer per se, but to the polymeric layer containing the auxiliary getter material.

As to the protective layer of hydrogen-permeable polymeric material the following polymers can be used: polysiloxanes such as polydimethylsiloxane, poli(methyl octyl siloxane), polyoxy(dimethyl)silylene, poly(methyl-1-pentenylene), polysiloxanes with hydroxilic or amminic terminations, polysulphones, poly alkanes, among which polyethylenes with different densities, polyether ether ketones, 25 polypyrrroles, polyurethanes, polyesters, polycarbonates, polyxylenes.

The polymers mentioned above are preferred for carrying out the invention, because they are compatible with applications having the major constraints in terms of compatibility of the materials employed and being at the same time mostly interesting, i.e. the use in electrochemical devices for energy storage.

Concerning the auxiliary getter material present in the protective polymeric membrane, this may be inserted by way of powders having a grain size not larger than 2

μm. In particular, getter materials having a nanometric size may also be advantageously used, i.e. with a maximum size comprised between 30 nm and 500 nm.

The wording “maximum size” has been used because the shape of the getter particles is typically irregular and not spherical.

5 Among the auxiliary getter materials suitable for carrying out the invention there are aluminum silicates, with particular reference to molecular sieves or zeolites, also having a modified structure, e.g. by amminic functionalization; oxides of alkaline earth metals; alkaline metal hydroxides, with particular reference to lithium hydroxide, or hydroxides of alkaline earth metals.

10 As getter materials suitable for the manufacturing of the supporting layer 11 zirconium, yttrium or titanium may be used, among which preferred is the use of titanium. These metals may also contain small amounts of other metal elements that do not significantly alter the characteristics of the supporting layer; typically, the level of these other metals must not exceed 20 wt%.

15 In a preferred embodiment the palladium or palladium-based composites directly coat the getter support surface that serves as a support for the multilayer system and are therefore in direct contact therewith. In an alternative embodiment it is also possible that an intermediate metallic layer is interposed between the getter material layer and the coating of palladium or palladium-based composites. The function of this layer is to 20 enhance the adhesion of the palladium or palladium-based composites layer, especially when electrochemical deposition processes for the palladium or palladium-based composites are used. Such an intermediate layer is preferably made of Ni, Cu, Pt, and typically has a thickness equal to or lower than 50 nm.

25 As to the thickness of the layers of the multi-layer composite getter, the thickness of the getter material layer having also the function of support for the improved multi-layer getter system may be comprised between 20 and 500, preferably between 100 and 300 micron (μm). As to the layer of palladium or palladium-based composites, the thickness may be comprised between 10 and 2000 nanometers (nm) and preferably between 20 and 250 nanometers.

30 As to the thickness of the external layer made of polymeric material, this must be comprised between 1 and 150 μm in order not to compromise the sorption speed of

hydrogen by the multi-layer composite getter and to ensure the absence of uncoated areas that might lead to the generation of hydrogen under anomalous operation conditions, i.e. in the presence of currents having reversed polarity.

Anyway, when an auxiliary getter material in a discrete form is used, i.e. in the 5 form of particulate, the thickness of the protective polymeric layer wherein the auxiliary getter material is dispersed must be at least twice the maximum size of the particulate.

In a second aspect thereof the invention relates to a method for the manufacturing 10 of a multi-layer composite getter according to the present invention, wherein the hydrogen-permeable polymeric layer protecting the deposit of the layer of palladium or palladium-based composites is deposited by spin coating, blading, or screen printing by starting from a mixture of the polymer and the auxiliary getter material.

In general, different techniques may be employed in order to deposit the 15 protective polymeric layer containing the auxiliary getter material on the layer of palladium or palladium-based composites. The important aspect associated with these techniques is that they can ensure a sufficient uniformity and regularity of the polymeric layer, in addition to ensure a sufficient adhesion between the layer of palladium or palladium-based composites and the polymeric layer.

Spin coating, blading and screen printing techniques are among the most suitable 20 techniques for the preparation of polymeric deposits having the required characteristics.

These techniques are not described herein, since they are widely known by those skilled 25 in the art.

As to the process for the formation of the intermediate layer made of palladium or palladium-based composites, particularly advantageous processes are sputtering, 25 thermal evaporation or evaporation by electron beam, electrochemical deposition processes or, alternatively, chemical deposition processes known in the field as "electroless", which do not require the passage of current, or processes that employ special inks containing palladium or palladium-based composites in solution.

In a third aspect thereof the invention relates to an electrochemical device for 30 energy storage that contains an electrolyte and a multi-layer composite getter according to the present invention.

In this case the protective polymeric layer must be insoluble in the electrolytic

solvent and impermeable to the electrolyte and its components.

In a preferred embodiment the permeability to hydrogen of the polymeric layer must be of at least one order of magnitude higher than the permeability to the electrolyte or to its components. Also in this case this property must be referred to the polymeric 5 layer containing the auxiliary getter material.

Particularly interesting devices among the electrochemical devices for energy storage are lithium batteries and electrolytic capacitors, with particular reference to "aluminum capacitors" and "supercapacitors".

Moreover, in this specific application the use of polydimethylsiloxane is very 10 advantageous.

Figure 4 shows a first way to use an improved multi-layer composite getter 10 within an electrochemical device 40 for energy storage comprising a hermetic container 41 whose electrodes are in the form of thin sheets wound to form a spiral 42, having a sectional view represented by close vertical parallel lines, impregnated with an 15 electrolyte (not shown). The electrical contacts 44, 44' connect the electrodes with the outside of the hermetic container. The improved multi-layer composite getter 10 is arranged in the central portion of this capacitor. The electrochemical device shown in figure 4 has a cylindrical geometry, but this geometry is not binding when putting into practice the invention. For example, parallelepiped is another preferred geometric shape 20 for these capacitors having the means for sorbing impurities placed in the central portion of the device.

Figure 5 shows a second embodiment of an electrochemical device 50 for energy storage. In this case the structure of the device 50 comprises wound electrodes forming a spiral 52 and impregnated with an electrolytic solution (not shown), these components 25 being enclosed in a hermetic container 51. An improved multi-layer composite getter 10 according to the present invention is arranged on one side of this capacitor.

In the embodiment of figure 5 the improved multi-layer composite getter is arranged along the whole inner edge of the device, but in a more general embodiment it may also be arranged along a portion only of the device.

Moreover, in some particular cases the devices may contain more composite 30 getter elements according to the present invention. For example, these may be present

both in the central portion and in the inner periphery of the device. Another very interesting variant is the embodiment of figure 6, which shows how the improved multi-layer getter 10 may be arranged in the bottom portion 63 of the hermetic container 51 of the electrochemical device 60.

5 This embodiment is not restrained to a cylindrical geometry, but may also be employed in other geometries, e.g. prismatic or parallelepiped.

#### EXAMPLE 1

In order to obtain a 10 w/w% filled membrane on a getter foil (Sample A), 3.0 g of nanozeolites (300 nm particle size) are dispersed in a 21.8g of a dimethyl siloxane, dimethylvinyl-terminated based resin and the resulting mixture is submitted to a mechanical stirring for 15 minutes. Then a residual pressure of 10-20 mm mercury is applied for 30 minutes in order to promote the material de-airing. Finally 2.2 g of dimethyl, methylhydrogen siloxane are added and the mixture is mechanically mixed 15 for additional 10 minutes.

The mixture is cast-deposited by using an automatic blade on a getter sample having foil shape with both surfaces active towards H<sub>2</sub>. Their typical size is about 2 cm x 5 cm. The metallic getter is a Ti foil 300 micron thick covered on both surfaces by 25 nm of Pd. The polymer protective layer (for sake of simplicity "membrane"), 20 micron thick and containing the auxiliary getter material, covers the whole available surface.

20 After spreading, the layer is cured at 120°C for 1h in order to promote the resin polymerization. Successively, the deposition process is repeated on the second layer of the support and an additional curing step at 120°C for 1h is applied. The sample was further annealed in vacuum for 2 hours at 200°C, to consolidate the membrane and 25 exposed to the atmosphere before H<sub>2</sub> sorption test. This allows the moisture to fill the membrane, in order to have conservative conditions for the sample (membrane occlusion by atmospheric moisture).

Using instead an amount of 6.6 g of nanozeolites in 26.4 g of resin or 10.8 g in 25.2 g getter foils were analogously obtained with 20 w/w% and 30 w/w% filled 30 membranes on getter foils (respectively Samples B and C)

## EXAMPLE 2

In order to obtain a 5 w/w% filled membrane on a getter foil (Sample D), 1.0 g of microzeolites (2  $\mu$ m particle size) are dispersed in a 19.0 g of a one-past silicone gel and the resulting mixture is submitted to a mechanical stirring for 30minutes. Then a residual pressure of 10-20 mm Hg is applied for 30 minutes in order to promote the material de-airing.

The mixture is cast-deposited on the first surface of a getter sample. After spreading, the layer is cured at 150°C for 1 hour in order to promote the resin polymerization. Successively, the deposition process is repeated on the second layer of the support and an additional curing step at 150°C for 1h is applied.

Using an amount of 2.0 of zeolites in 18.0 g of gel (and similarly 4.0 g in 16.0 g, 6.0 g in 14.0 g, or 10.0 g in 10.0 g) getter foils were analogously obtained with 10 w/w%, 20 w/w%, 30 w/w% and 50 w/w% filled membranes on getter foils (respectively Samples E, F, G and H)Each Sample (A to H) was singularly mounted into a sorption bench and after short evacuation time (about 1 minute) the sorption test started. The sorption test ran for almost 24 hours. Tests were made at room temperature, at a constant pressure of 8 torr over the samples.

Slope (that is the sorption speed of the getter system at the beginning of the sorption test) and the sorbed hydrogen amount after 24 hours are reported in table 1 for all the samples prepared according to the present invention. The sorption properties in function of the different filling of the membrane show an unexpected maximum value with 20 w/w% concentrations and acceptable value up to 50 w/w% concentrations.

Sample	Slopes ( $10^{-3} \text{ m}^3 \cdot \text{Pa} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$ )	Total sorbed amount (after 24hr) ( $\text{Pa} \cdot \text{m}^3$ )
A (nano 10%)	13.3	1163
B (nano 20%)	17	1519
C (nano 30%)	9.5	1000
D (micro 5%)	14.4	1232
E (micro 10%)	10.8	825
F (micro 20%)	18.3	1512
G (micro 30%)	15.7	1313
H (micro 50%)	7.8	737

## CLAIMS

1. Multi-layer composite getter (10; 20; 30) for hydrogen removal comprising a support (11) made essentially of a metallic getter material, with two surfaces (12, 12'), wherein a layer of palladium or palladium-based composites (13, 13') is provided on at least one of said surfaces defining a coated surface, wherein a polymeric protective layer permeable to hydrogen (14, 14') is provided on at least 5 80% of the surface of the coated surface, characterized in that one or more auxiliary getter materials (15) are dispersed in said polymeric protective layer permeable to hydrogen with a weight concentration comprised between 5 wt% and 50 wt%, calculated on the overall weight of the polymeric layer containing the auxiliary getter materials.  
10
2. Multi-layer composite getter according to claim 1, wherein said weight concentration of auxiliary getter materials is comprised between 15 wt% and 30 wt%.  
15
3. Multi-layer composite getter according to claim 1, wherein said layer of palladium or palladium-based composites is in direct contact with the support.
4. Multi-layer composite getter according to claim 1, wherein between said layer of palladium or palladium-based composites and said support a metallic layer is  
20 present.
5. Multi-layer composite getter according to claim 1, wherein said layer of palladium or palladium-based composites is provided on both surfaces of the support made essentially of a metallic getter material.
6. Multi-layer composite getter according to claim 1, wherein said layer of palladium or palladium-based composites is disposed on only one surface of the support made essentially of metallic getter material.  
25
7. Multi-layer composite getter according to claim 1, wherein said layer of palladium

or palladium-based composites covers at least 80% of the surface of the coated surface.

8. Multi-layer composite getter according to claim 1, wherein said polymeric protective layer permeable to hydrogen containing an auxiliary getter material has a hydrogen permeability equal to or higher than  $10^{-12} \text{ cm}^3 \text{ cm cm}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$  at 25° C, 1 bar.
9. Multi-layer composite getter according to claim 1, wherein said polymeric protective layer permeable to hydrogen is made with polysiloxanes, polisiloxanes with hydroxilic or amminic terminations, polysulphones, poly alkanes, polyether ether ketones, polypyrrroles, polyurethanes, polyesters, polycarbonates, polyxylenes.
10. Multi-layer composite getter according to claim 1, wherein said getter material is made of at least 80% by weight of a metal chosen among zirconium, yttrium, titanium.
11. Multi-layer composite getter according to claim 1, wherein said palladium-based composites comprise at least 60% by weight of palladium and are chosen among Pd-Ag, Pd-Cu, Pd-V, Pd-Ni.
12. Multi-layer composite getter according to claim 1, wherein the thickness of said support made essentially of a getter material is comprised between 20  $\mu\text{m}$  and 500  $\mu\text{m}$ .
13. Multi-layer composite getter according to claim 1, wherein the thickness of said layer of palladium or palladium-based composite is comprised between 10 and 2000 nm.
14. Multi-layer composite getter according to claim 1, wherein the thickness of said polymeric protective layer permeable to hydrogen is comprised between 1  $\mu\text{m}$  and 150  $\mu\text{m}$ .

15. Multi-layer composite getter according to claim 1, wherein said auxiliary getter material comprises one or more materials chosen among aluminosilicates, with particular reference to molecular sieves or zeolites, functionally modified aluminosilicates, alkaline-earth metal oxides; alkali metal hydroxides with particular reference to lithium hydroxide, alkaline-earth metal hydroxides.
16. Multi-layer composite getter according to claim 15, wherein said functional modification is amminic.
17. Multi-layer composite getter according to claim 1, wherein said auxiliary getter material is used in discrete form.
- 10 18. Multi-layer composite getter according to claim 17, wherein said auxiliary getter material in discrete form is in form of particulate having maximum size of 2  $\mu\text{m}$ , and more preferably having maximum dimension comprised between 30 nm and 500 nm.
- 15 19. Multi-layer composite getter according to claim 18, wherein the thickness of said protective polymeric layer permeable to hydrogen is at least twice the maximum size of said auxiliary getter material in form of particulate.
- 20 20. Energy storage electrochemical device (40; 50; 60) containing an electrolyte and its components, and one or more multi-layer composite getters (10) according to claim 1, enclosed in a hermetic container (41; 51).
- 20 21. Energy storage electrochemical device according to claim 20, wherein said polymeric protective layer permeable to hydrogen is impermeable to the electrolyte and its components.
- 25 22. Energy storage electrochemical device according to claim 20, wherein said multi-layer composite getter is arranged in one or more of the following positions: central part, along surface walls, bottom or upper portions.
23. Energy storage electrochemical device according to claim 20, wherein said device

is a lithium battery.

24. Energy storage electrochemical device according to claim 20, wherein said device is a supercapacitor.

25. Energy storage electrochemical device according to claim 20, wherein said device  
5 is an electrolytic capacitor.

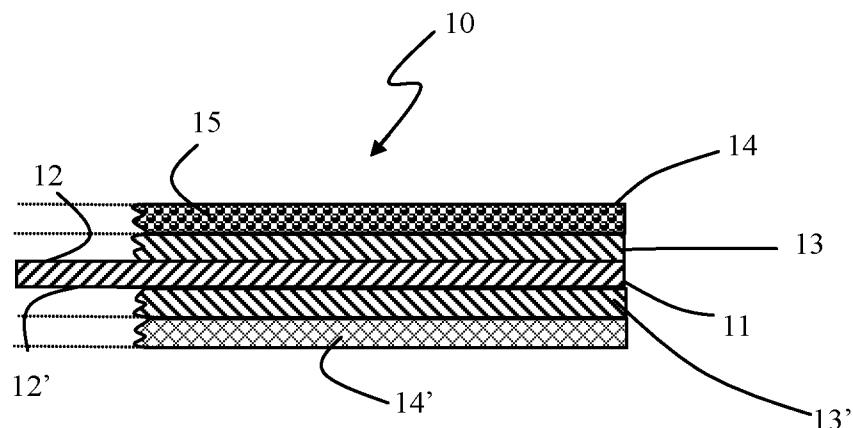


Fig. 1

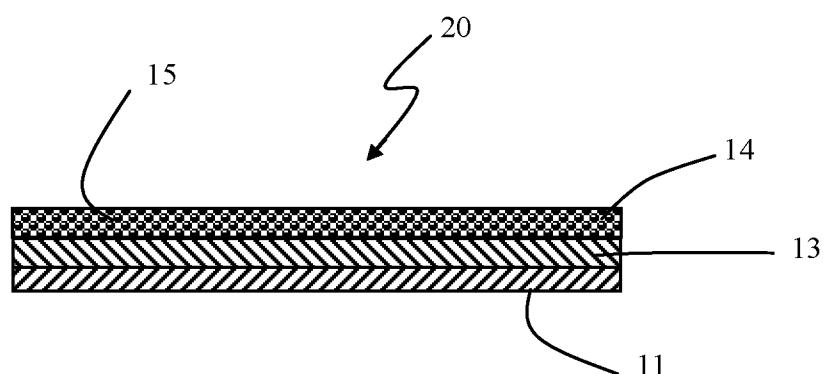


Fig. 2

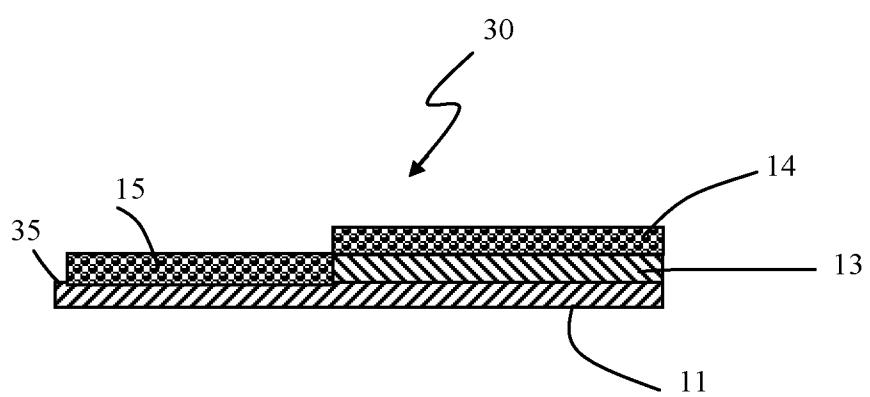
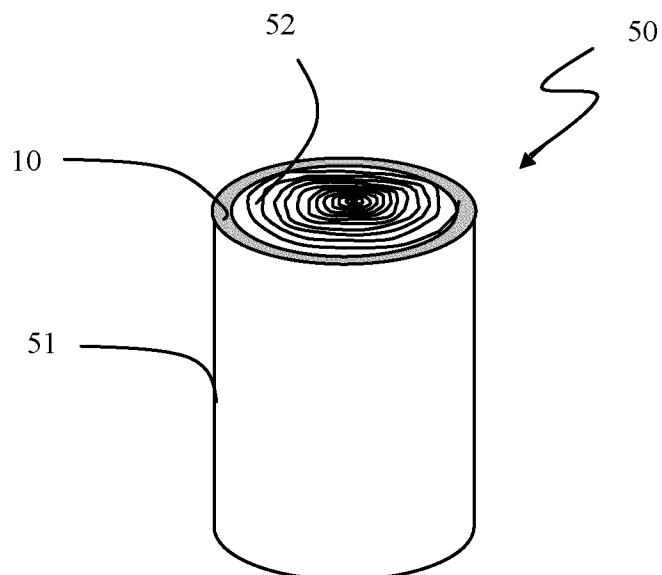
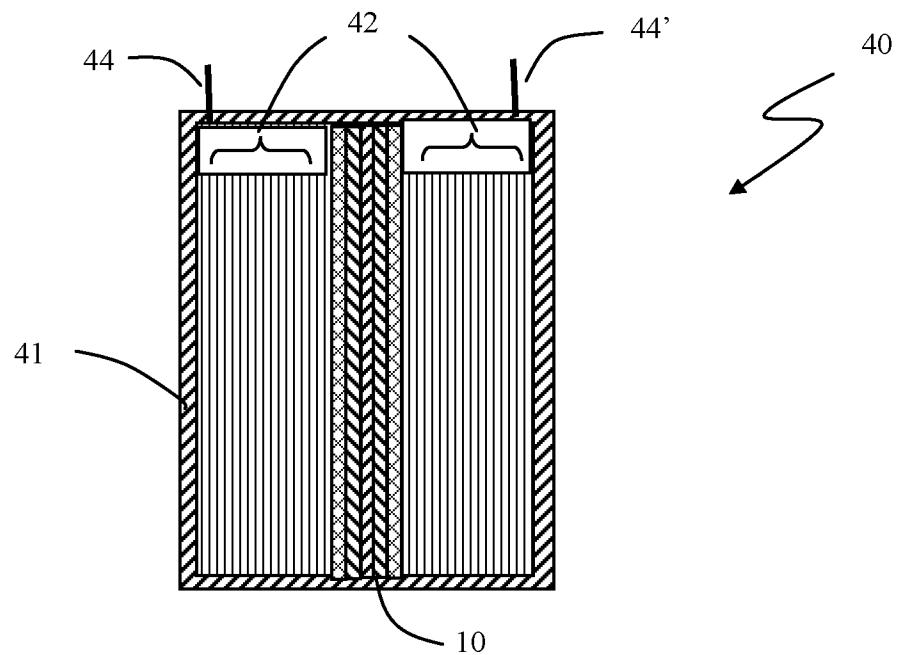
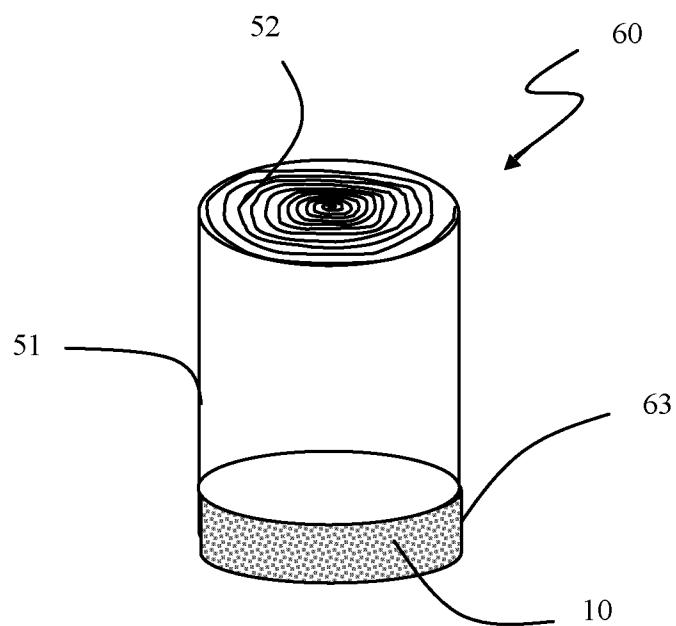


Fig. 3





**FIG. 6**

# INTERNATIONAL SEARCH REPORT

International application No  
PCT/EP2011/069819

**A. CLASSIFICATION OF SUBJECT MATTER**  
INV. C01B3/00 C01B3/50  
ADD.

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)  
C01B

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 practical, search terms used)

EPO-Internal, WPI Data

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>WO 2008/033560 A2 (GETTERS SPA [IT]; PETERSEN RONALD O'DELL [US]; KULLBERG RICHARD C [US]) 20 March 2008 (2008-03-20) abstract claims 2,8,38 figure 1 page 16, lines 7-24</p> <p>-----</p> <p>WO 2006/089068 A2 (GETTERS SPA [IT]; KULLBERG RICHARD [US]; ARMSTRONG TIM [US]; CONTE AND) 24 August 2006 (2006-08-24) abstract claims 1,2,13-17,21</p> <p>-----</p> <p>-/-</p>	1-25
A		1-25

Further documents are listed in the continuation of Box C.

See patent family annex.

\* Special categories of cited documents :

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- "P" document published prior to the international filing date but later than the priority date claimed

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
1 December 2011	12/12/2011
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer  Alvarez Rodriguez, C

## INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2011/069819

## C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2007/080614 A1 (GETTERS SPA [IT]; TOIA LUCA [IT]; AMIOTTI MARCO [IT]) 19 July 2007 (2007-07-19) abstract claims 1,7,8,22 page 3, lines 11-17 page 4, lines 4-11 page 5, lines 3-6, 10-16 ----- WO 03/028096 A2 (RAYTHEON CO [US]) 3 April 2003 (2003-04-03) abstract claims 1-3,5 -----	1-25
A		1-25

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2011/069819

Patent document cited in search report	Publication date	Patent family member(s)			Publication date
WO 2008033560	A2 20-03-2008	AU 2007294684 A1 CA 2663111 A1 CN 101523532 A EP 2080205 A2 JP 2010503992 A KR 20090053957 A RU 2009113558 A US 2009237861 A1 WO 2008033560 A2 ZA 200901741 A			20-03-2008 20-03-2008 02-09-2009 22-07-2009 04-02-2010 28-05-2009 20-10-2010 24-09-2009 20-03-2008 30-06-2010
WO 2006089068	A2 24-08-2006	AT 518804 T CN 101163586 A EP 1851050 A2 JP 2008529792 A KR 20070120499 A KR 20100040332 A US 2009215610 A1 WO 2006089068 A2			15-08-2011 16-04-2008 07-11-2007 07-08-2008 24-12-2007 19-04-2010 27-08-2009 24-08-2006
WO 2007080614	A1 19-07-2007	AU 2006335652 A1 CA 2628246 A1 CN 101313379 A EP 1974360 A1 JP 2009524213 A US 2008310079 A1 WO 2007080614 A1			19-07-2007 19-07-2007 26-11-2008 01-10-2008 25-06-2009 18-12-2008 19-07-2007
WO 03028096	A2 03-04-2003	EP 1430527 A2 IL 156227 A US 2003062610 A1 US 2004106001 A1 WO 03028096 A2			23-06-2004 24-12-2009 03-04-2003 03-06-2004 03-04-2003