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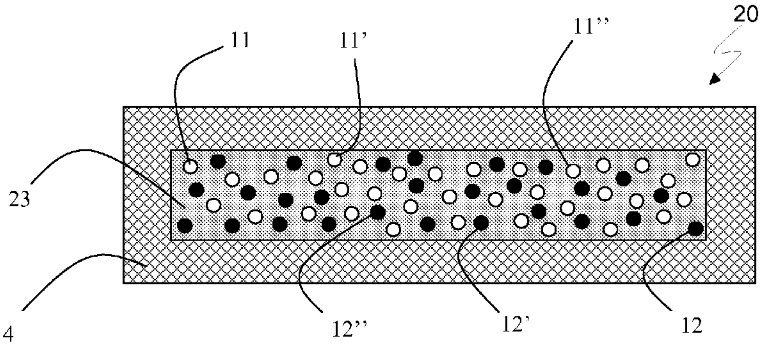


Fig.2

(57) Abstract: Improved carbon dioxide composite getter (20) comprising a CO$_2$-permeable envelope (14) containing powders of two active materials (11, 11', 11'', 12, 12', 12'')and sealed systems employing such improved carbon dioxide composite getter.

CARBON DIOXIDE COMPOSITE GETTER

The present invention in a first aspect thereof is inherent to an improved carbon dioxide composite getter and in a second aspect thereof to sealed systems employing such an improved carbon dioxide composite getter.

Nowadays there is a whole class of sealed systems where the presence of carbon dioxide is detrimental, both in terms of negative impact due to chemical interactions of the carbon dioxide with one or more components present in the sealed system, or as a consequence of a physical interaction. Non-limiting examples of systems negatively affected by chemical interactions are organic electronic devices, while examples of the latter type of devices where is the physical interaction to determine a device deterioration, are typically the ones where CO_2 is produced by the systems themselves as a side effect of their operation, and this may lead to overpressure and consequent rupture of the device case.

Among the most important devices of these types there are the energy storage systems such as rechargeable lithium batteries, and the detrimental role and risks posed by CO_2 are described in various articles such as “In situ study on CO_2 evolution at lithium-ion battery cathodes", by Vetter et al., published in the Journal of Power Sources 159 (2006) 277-281, “Gas evolution behaviors for several cathode materials in lithium-ion batteries", by Kong, published in the Journal of Power Sources 142 (2005) 285–291 and “Effect of Li_2CO_3 additive on gas generation in lithium-ion batteries", by Shin et al, published in the Journal of Power Sources 109 (2002) 47–52.

Rechargeable lithium batteries are among the most critical devices since carbon dioxide overpressure may lead to sudden rupture of the device case with the risk of leakage of flammable substances (the electrolytes contained therein). This problem is also enhanced by the fact that typically the free volume in these devices is very small, whereby the generation of low quantities of carbon dioxide will lead to a quick rise in the device internal pressure.

In the following, reference will be made specifically to the use of CO_2 getter systems in this type of devices in view of this particular critical aspect, even though, as outlined above, the presence of CO_2 and consequently the need for its efficient removal is shared by many different sealed systems.

The problem of the removal of gaseous impurities in lithium batteries is described and addressed in WO 2008/148778 and WO 2008/148781, both in the applicant's name. In these documents the main aspect addressed is the compatibility of the getter materials with the electrolytic environment of the battery. One of the problems described in these documents with regards to the use of alkali metal hydroxide for CO_2 removal is the concurrent release of H_2O and therefore the need to remove it in order to avoid a shifting of the problem from carbon dioxide to H_2O. This leads to bulkier systems or systems that have a limited capacity for CO_2, since a significant part of the available volume needs to be taken up by the moisture absorber.

The purpose of the present invention is to provide an improved carbon dioxide composite getter comprising an envelope permeable to CO_2 defining an internal volume V, that contains powders of a first and a second active materials whose cumulative volume is Vm, characterized in that said first active material is lithium hydroxide and said second active material is lithium oxide, and the $LiOH/Li_2O$ molar ratio is comprised between 0,05 and 1,5

By cumulative volume Vm it is meant the overall sum of the active materials (lithium oxide and lithium hydroxide) particles volume contained within the internal volume V defined by the CO_2-permeable envelope.

The molar ratio is preferably comprised between 0,05 and 0,2 for all those applications where the composite getter sorption speed is less important and that instead require higher CO_2 capacity, while a ratio comprised between 0,2 and 0,7 would provide a compromise solution between optimal CO_2 sorption speed and CO_2 removal capacity, and when the ratio is comprised between 0,7 and 1,5 the getter has its sorption speed optimized.

By CO_2-permeable envelope it is meant a material that has a CO_2 permeation coefficient of at least 50 $cm^3*mm/(m^2*day*atm)$, said value being preferably equal to or higher than 100. At the same time the CO_2-permeable envelope preferably usefully exhibits a moisture vapor transmission rate (MVTR) that is not higher than 0,6 $g*mm/(m^2*day)$.

The invention will be also described with the help of the following figures where:

- Figure 1 shows a cross section view of a first embodiment of a CO_2 composite getter system according to the present invention,

- Figure 2 shows a cross section view of a second embodiment of a CO_2 composite getter system according to the present invention,

- Figures 3 and 4 show a performance comparison between getter systems made according to the present invention and solutions not encompassed by it.

In the figures the dimensions and dimensional ratio of the depicted elements, with particular and non-exclusive reference to the dimensions of the active material particles, are not correct but have been altered in order to improve their readability.

The inventors have found that with the improved getter systems according to the present invention there is an advantage given by the fact that the moisture sorber (Lithium oxide) after the H_2O capture becomes a CO_2 sorber, according to the following reaction:

$$Li_2O + H_2O \rightarrow 2LiOH \qquad (I)$$

In particular the lithium hydroxide reacts with carbon dioxide according to the following reaction:

$$2LiOH + CO_2 \rightarrow Li_2CO_3 + H_2O \qquad (II)$$

The above reaction (II) shows why in the above mentioned patent applications WO 2008/148778 and WO2008/148781 reference is made to the need of an associated moisture absorber.

The inventors have surprisingly and unexpectedly found that such combination of materials requires also additional conditions in order to be an effective CO_2 getter; in particular the novel combination of active materials according to the present invention, i.e. lithium hydroxide combined with an excess of lithium oxide, shall be confined in a volume, smaller than the volume of the sealed device, by means of a CO_2-permeable envelope. Such volume, together with the characteristic and behavior of the CO_2-permeable envelope provides the appropriate environment for CO_2 capture (as per reaction II) and for the conversion of lithium oxide into lithium hydroxide (as per reaction I).

In particular there are two main embodiments for the carbon dioxide composite getter according to the present invention.

In a first embodiment the lithium hydroxide and lithium oxide powders are mixed together and put into a CO_2-permeable “pouch” that is sealed, for example, by heating.

In a preferred solution the ratio of the active material volume Vm to the getter system internal volume V is comprised between 0,15 and 0,9.

In a second embodiment the CO_2 composite getter comprises a dispersion in a suitable polymeric binder of lithium hydroxide and lithium oxide in the correct ratio, as above defined, which is in contact with a CO_2-permeable envelope, as per definition provided above. In this case it is possible that the CO_2-permeable envelope, although defining an internal volume V, does not completely surround the polymeric binder, i.e. a small portion of the binder containing the first and second active materials is not covered by the envelope. In fact in this case also the binder defines the internal volume V. It is important that only a small fraction of the binder is not covered/coated with the CO_2-permeable envelope, i.e. 95% or higher of the polymeric binder surface is encased by the CO_2-permeable envelope. It is important to remark that the internal volume in this case is equivalently and sufficiently defined both by the envelope covering at least 95% of the surface area of the binder and therefore defining an internal volume presenting a small aperture, as well as the binder with the active material powders that represents the internal volume.

Even though a small aperture in the CO_2-permeable envelope is tolerable and does not impair significantly the technical features of the composite getters, it is preferred also in this case to have a closed envelope, as per the use of the active materials in powders form (without the binder).

In this embodiment the level of loading of the powders into the polymeric binder assures the presence of an optimized “reaction volume” for the powders of the two active materials and in particular this condition is achieved when the overall loading level for the LiOH and Li_2O powders into the polymeric binder is comprised between 20 and 60 wt%, and preferably comprised between 40 and 50 wt%.

Therefore with the getter systems according to the present invention the additional element for H_2O removal is actually a “precursor” for the CO_2 adsorber, resulting in a system having a higher capacity with respect to systems associating the lithium hydroxide with a generic moisture removing material. At the same time the structure of the getter system according to the present invention is one that while providing a suitable reaction volume renders the CO_2 sorption characteristics suitable to control the pressure within sealed devices, by providing a good capacity coupled with an appropriate reaction kinetics.

It is to be remarked that this result is something that is accomplished by the getter system according to the present invention as a whole, in fact it has been verified that if the powders or lithium hydroxide and lithium oxide in the correct ratio are just mixed together and put into a big volume for testing (simulating a situation where the powders are directly placed in the sealed device without the confining effect of the enclosing CO_2-permeable envelope) the system shows a negligible capacity.

A cross-sectional view of a composite CO_2 getter system 10 according to the present invention is shown in Figure 1, showing particles of lithium oxide 11, 11', 11'' (white circles), and of lithium hydroxide 12, 12', 12'' (black circles), surrounded by a CO_2 permeable envelope 14. The system 10 presents an internal free volume 13 (indicated in white).

Lithium oxide particles and lithium hydroxide particles are represented as circles even though in reality and in the most common cases their shape is not regular. Also the getter system 10 has been depicted with a regular and rectangular shape, but any shape is possible, since the object of the present invention is a system containing mixed powders of two active materials (lithium oxide and lithium hydroxide) enclosed in a suitable envelope defining a volume V, only partially filled by such powders.

Figure 2 shows a cross-sectional view of an alternate embodiment of a composite getter system 20 in which, differently from the system shown in Figure 1, the lithium oxide particles 11, 11', 11'' and lithium hydroxide particles 12, 12', 12'' are dispersed in a polymeric binder 23, indicated in grey.

The systems shown in Figure 1 and Figure 2 are therefore different from what is described in the US patent 3,684,712 that discloses granules of lithium oxide surrounded by a shell of an alkaline-earth metal oxide, the differences residing both in the nature of the materials, with reference to the materials associated to lithium hydroxide, and in the configurations, since US 3,684,712 discloses composite granules and not a dispersion in a suitable binder enclosed in a permeable envelope.

In both preferred embodiments according to the present invention the employed powders have dimensions that are usually determined and controlled by means of a sieving operation, and owing also to the geometrical conformation of the powders (not regular/spherical), this ensures that are selected and employed all the powders that have a minimal size lesser than the sieve opening.

In the present invention, for both active materials when they are employed as such, are usefully employed particles/powders whose minimal size is higher than 1 μm. In case of getter powders dispersed in a polymeric binder, such as in the embodiment shown in figure 2, the preferred powders distribution is comprised between 1 and 250 μm (minimal size of the powders), this allows for an easier manufacturability of systems with the desired thicknesses.

With regards to embodiments envisioning the use of a polymeric binder particularly advantageous is the use of High Density Polyethylene (HDPE) or Polypropylene (PP), Low Density Polyethylene (LDPE), copolymer ethylene-octene, polyolefin modified with maleic anhydride, Ethylene Vinyl (EVA), Styrene-Ethylene-Butadiene-Styrene (SEBS), Ethylene Propylene Diene Monomer (EPDM), Thermoplastic Elastomer (TPE) and combinations thereof.

The thickness of the carbon dioxide permeable envelope is usefully comprised between 5 and 500 μm. It is to be underlined that such thickness represents the mean value, since certain points of the envelope (sealing regions) may present a different thickness (typically higher).

The thickness of the binder containing the powders shall be comprised between 50 and 400 μm, and in any case shall not be less than at least 1,5 times the minimum dimension of the employed powders.

In general the same materials listed above as binders may also be used to make the enclosing CO_2-permeable envelope for both embodiments (free powders, polymer bound powders), in certain more demanding applications, such as in the case of rechargeable lithium batteries, the use of High Density PolyEthylene (HDPE) and PolyPropylene (PP) being preferred.

As outlined above when the composite getter systems according to the present invention are used and placed within the sealed systems, there is a continuous shift in the ratio between lithium hydroxide and lithium oxide, with the former becoming more and more preponderant toward the end of the system. This continuous shift corresponds to the fact that the lithium hydroxide is consumed by carbon dioxide and forms lithium carbonate as per reaction (II) and concurrently lithium oxide becomes lithium hydroxide as per reaction (I).

So the $LiOH/Li_2O$ molar ratio for the getter systems according to the present invention is to be evaluated, considered and determined for a “fresh” getter system, i.e. a getter system not yet exposed to high levels of CO_2 (and therefore consumed). The getter systems according to the present invention are the ones that exhibit the correct ratio between lithium hydroxide and lithium oxide when the molar content of lithium carbonate over the sum of the lithium oxide and lithium hydroxide is less then 25%.

A preferred solution for the getter system according to the present invention envisions the use of a drying element, that advantageously is made by a dispersion of a moisture sorber in a suitable binder, e.g. a polymeric matrix. This further ensures that toward the end of the life there is no moisture release from the CO_2 getter system. It is to be underlined that the amount of the moisture sorber added in this case is much smaller than in other conventional systems when the lithium hydroxide is associated with another moisture-sorbing element.

In particular the following configurations for the sealing element of the getter system are possible:

- powders of the moisture sorber directly dispersed in the external envelope (1-layer system)
- powders of the moisture sorber dispersed in an additional layer external to the CO_2-permeable envelope (2-layers system)
- powders of the moisture sorber dispersed in an additional layer external to the CO_2-permeable envelope that is shielded from the device environment by means of another polymeric layer (3-layers system).

Suitable materials for the H_2O removal are for example alkaline-earth metal oxides, with particular reference to MgO, CaO and aluminosilicates, such as zeolite.

In a second aspect thereof the invention consists in a sealed system containing an improved CO_2 composite getter comprising a CO_2-permeable envelope having an internal volume V, containing powders of a first and a second active materials, characterized in that said first active material is lithium hydroxide and said second active material is lithium oxide, and the LiOH/Li_2O molar ratio is less than 1,5.

In a preferred embodiment said sealed systems are energy storage devices such as rechargeable Li-Ion batteries and supercapacitors.

In an even more preferred embodiment the CO_2 getter system contains between 5 and 500 milligrams of active material powders, such quantity may be higher and scale up depending also on the size of the sealed system, for example rechargeable Li-Ion batteries or supercapacitors may vary greatly in their internal volume and therefore need and can accommodate a higher quantity of getter material.

The invention will be further illustrated with the help of the following non-limiting examples.

Example 1

A getter system according to the present invention was made by mixing 11,5 milligrams of LiOH and 34,5 milligrams of Li_2O powders (minimum size less than 100 μm) and putting them in a CO_2-permeable envelope made of HDPE, with a thickness of 10 μm. The internal Vm/V ratio was 0,25.

This getter system was then put in a Hiden microgravimetric balance thermostated at 25°C, kept in vacuum by a turbomolecular vacuum pump for 2 hours for system conditioning, and then exposed to 1 bar of CO_2 and its weight increase monitored and recorded by means of the microgravimetric balance. The results of this test are shown in Figure 3, line 1.

The same experiment was repeated by placing the same powders mixture directly in the microbalance and repeating the CO_2 exposure test. This condition simulates the use of the powders in the correct ratio directly in the device, without the presence (and therefore the effects) of the enclosing CO_2-permeable envelope. The results of this test are shown in Figure 3, line 2.

The comparison of these data shows that a mix of powders has almost a negligible CO_2 sorption capacity with respect to a getter system according to the present invention using the very same materials combination in the very same ratio.

Example 2

In this case a 47 wt% dispersion of $LiOH+Li_2O$ in HDPE is produced in an extruder. A sample according to the present invention is made by enclosing an extruded sample of 53,5 mg and 1 x 1,5 cm x 230 μm in size in a 10 μm-thick HDPE envelope and its weight increase after CO_2 exposure, as per Example 1, is monitored and recorded. The results of this tests are shown in Figure 4, dotted line 3.

Similarly a sample is made and tested as per the previous experiment, but in this case the sample does not have the CO_2-permeable enclosing envelope. The results of this test shown in Figure 4, continuous line 4.

This test shows that by adding the polymeric envelope there is a increase in the amount of removed CO_2 corresponding to a 10% wt increase.

CLAIMS

1. Carbon dioxide composite getter (10; 20) comprising a CO_2-permeable envelope (14), defining an internal volume V, that contains powders of a first and a second active materials (11, 11’, 11’’, 12, 12’, 12’’) whose cumulative volume is Vm, characterized in that said first active material is lithium hydroxide (12, 12’, 12’’) and said second active material is lithium oxide (11, 11’, 11’’), and the $LiOH/Li_2O$ molar ratio is comprised between 0,05 and 1,5, preferred sub-ranges of said molar ratio being respectively between 0,05 and 0,2 for higher CO_2 removal capacity, between 0,7 and 1,5 for higher sorption speed and between 0,2 and 0,7 for a compromise between said two characteristics.

2. Carbon dioxide composite getter according to claim 1, wherein the active materials (11, 11’, 11’’, 12, 12’, 12’’) are in the form of free powders and the ratio between Vm and V is comprised between 0,15 and 0,9.

3. Carbon dioxide composite getter according to claim 1 or 2, wherein said powders minimal size is higher than 1 μm.

4. Carbon dioxide composite getter according to any of the preceding claims, wherein the CO_2-permeable envelope (14) has a CO_2 permeation coefficient of at least 50 $cm^3*mm/(m^2*day*atm)$, preferably higher then 100 $cm^3*mm/(m^2*day*atm)$,

5. Carbon dioxide composite getter according any of the preceding claims, wherein the CO_2-permeable envelope (14) exhibits a moisture vapor transmission rate not higher than 0,6 g $*mm/(m^2*day)$.

6. Carbon dioxide composite getter according to any of the preceding claims, wherein said CO_2-permeable envelope (14) is made with a material selected among High Density Polyethylene (HDPE), Polypropylene (PP), Low Density Polyethylene (LDPE), copolymer ethylene-octene, polyolefin modified with maleic anhydride, Ethylene Vinyl Acetate (EVA), Styrene-Ethylene-Butadiene-Styrene (SEBS), Ethylene Propylene Diene Monomer (EPDM), Thermoplastic Elastomer (TPE) and combinations thereof.

7. Carbon dioxide composite getter according to any of the preceding claims, wherein said CO_2-permeable envelope (14) has a thickness comprised between 5 and

500 μm.

8. Carbon dioxide composite getter according to any of the preceding claims, further comprising a moisture sorber arranged outside said CO_2-permeable envelope (14).

9. Carbon dioxide composite getter according to claim 8, wherein said moisture sorber comprises a dispersion in a polymeric matrix of a moisture-removing material that preferably comprises one or more of alkaline-earth metal oxides and aluminosilicates.

10. Carbon dioxide composite getter according to claim 1 or any of claims 3 to 9, wherein said powders of active materials (11, 11', 11'', 12, 12', 12'') are dispersed in a polymeric binder (23).

11. Carbon dioxide composite getter according to claim 10, wherein said polymeric binder (23) is selected among High Density Polyethylene (HDPE), Polypropylene (PP), Low Density Polyethylene (LDPE), copolymer ethylene-octene, polyolefin modified with maleic anhydride, Ethylene Vinyl (EVA), Styrene-Ethylene-Butadiene-Styrene (SEBS), Ethylene Propylene Diene Monomer (EPDM), Thermoplastic Elastomer (TPE) and combinations thereof.

12. Carbon dioxide composite getter according to claim 10 or 11, wherein said powders minimal size is comprised between 1 and 250 μm.

13. Carbon dioxide composite getter according to any of claims 10 to 12, wherein the content of said active materials powders (11, 11', 11'', 12, 12', 12'') in said polymeric binder (23) is comprised between 20 and 60 wt%, preferably between 40 and 50 wt%.

14. Carbon dioxide composite getter according to any of claims 10 to 13, wherein the thickness of the binder (23) containing the powders (11, 11', 11'', 12, 12', 12'') is comprised between 50 and 400 μm, and in any case is not less than at least 1,5 times the minimum dimension of the employed powders.

15. Carbon dioxide composite getter according to any of the preceding claims, wherein the amount of active material powders (11, 11', 11'', 12, 12', 12'') is comprised between 5 and 500 milligrams.

16. Sealed system comprising a carbon dioxide composite getter according to any

of the preceding claims.

17. Sealed system according to claim 16, wherein said system is an energy storage device, preferably a rechargeable Li-Ion battery or a supercapacitor.

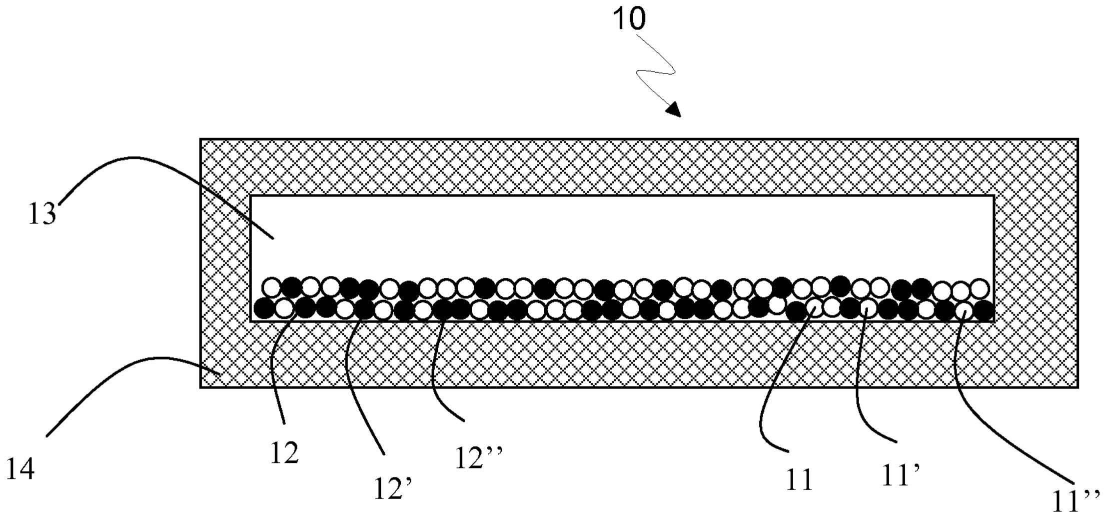


Fig.1

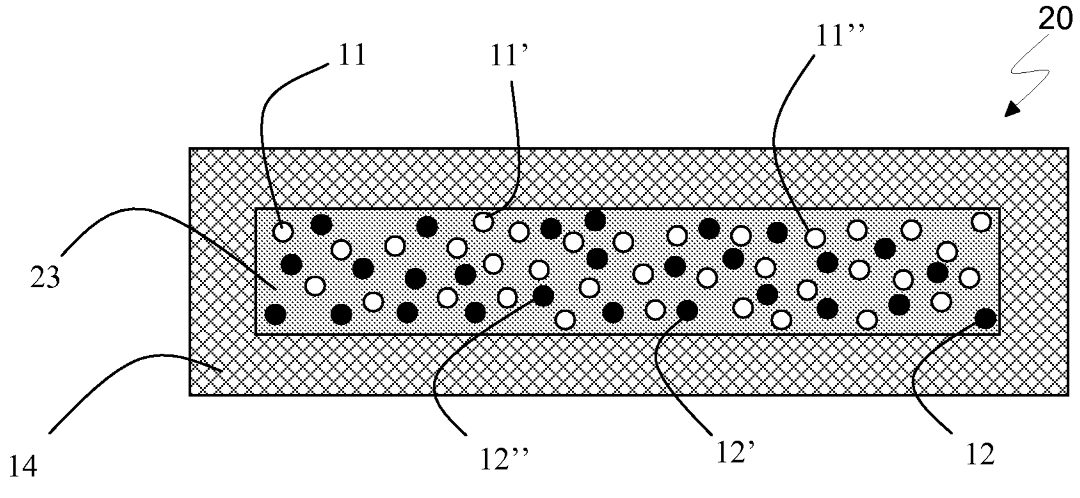


Fig.2

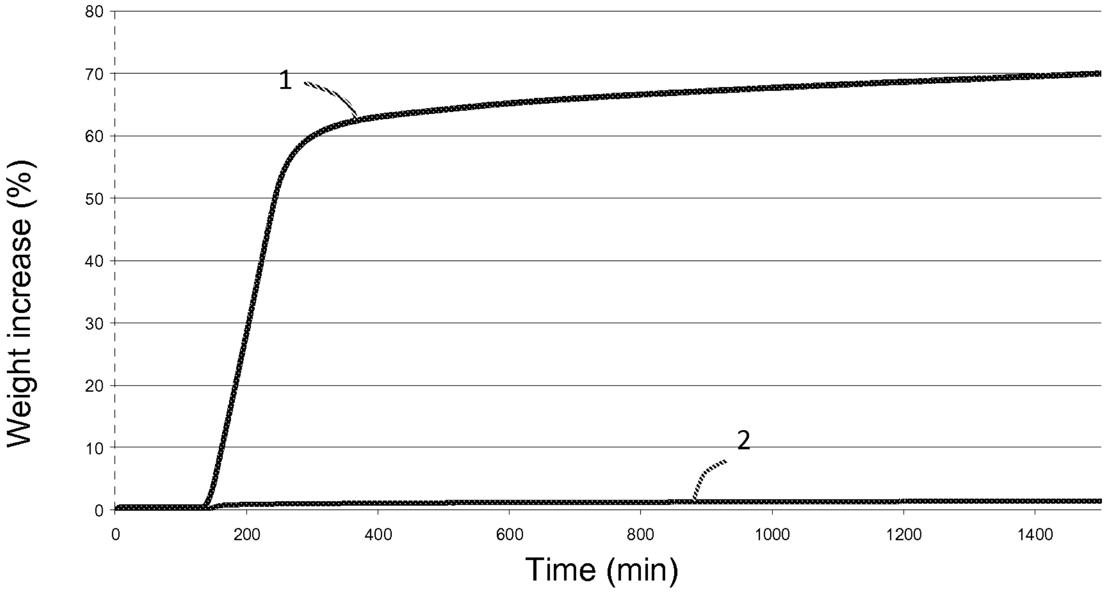
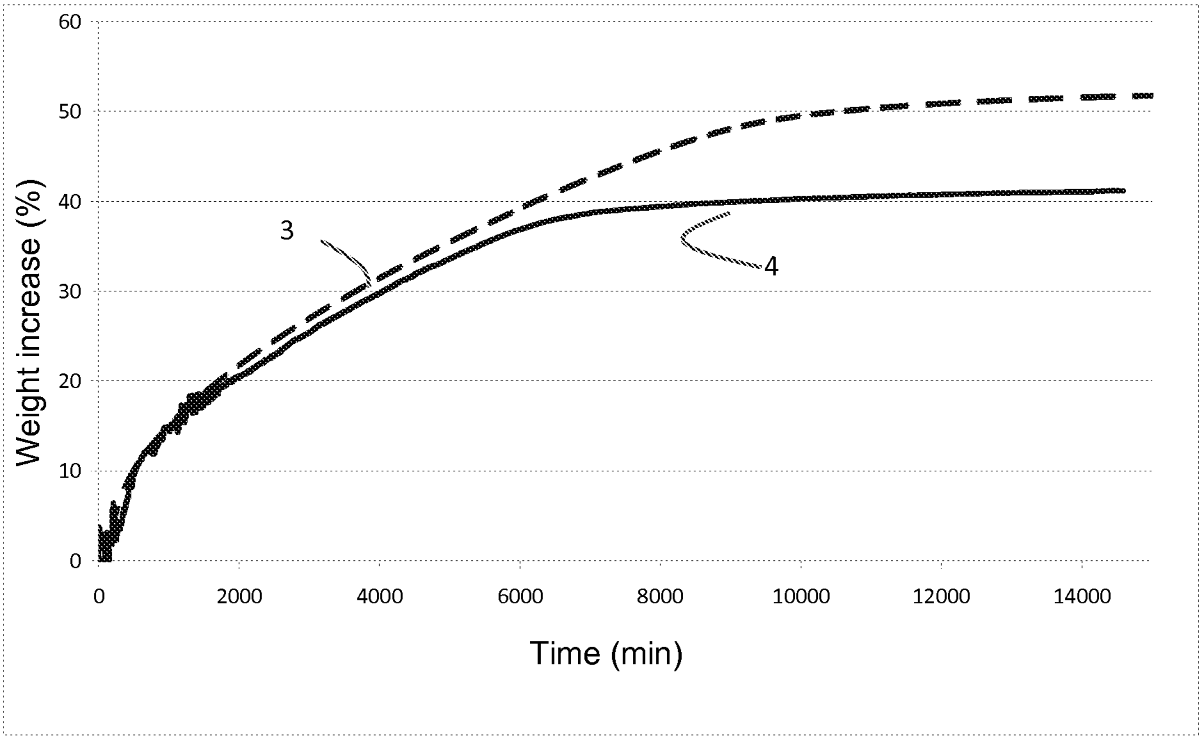

80
70
60
50
40
30
20
10
0
Weight increase (%)
1
2
0
200
400
600
800
1000
1200
1400
Time (min)

Fig.3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40
30
20
10
0
Weight increase (%)
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4
0
2000
4000
6000
8000
10000
12000
14000
Time (min)

Fig.4