(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 2 130 940 A1

(12) EUROPEAN PATENT APPLICATION

(43) Date of publication:
09.12.2009 Bulletin 2009/50

(51) Int Cl.:
C23C 14/24 *(2006.01)*

(21) Application number: **08009925.2**

(22) Date of filing: **30.05.2008**

(84) Designated Contracting States:
AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MT NL NO PL PT RO SE SI SK TR
Designated Extension States:
AL BA MK RS

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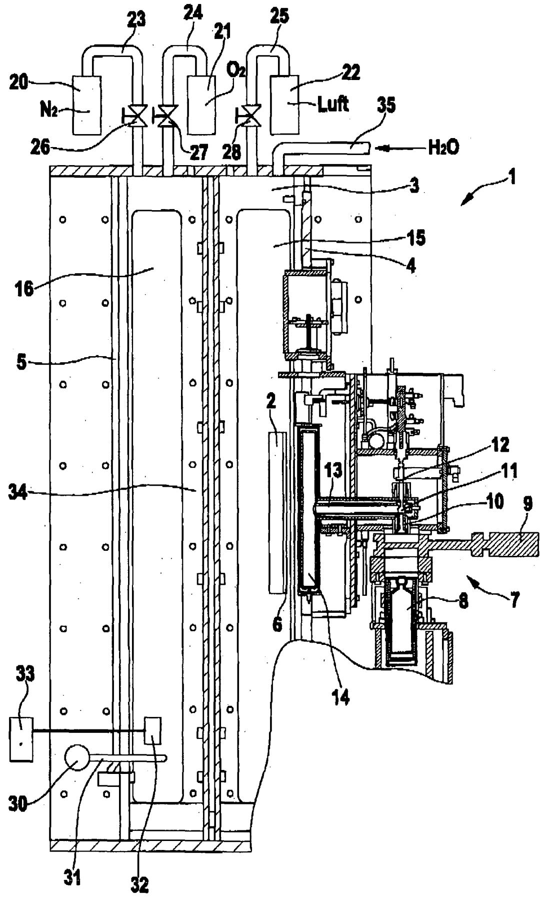
(54) Arrangement and method for removing alkali- or alkaline earth-metals from a vacuum coating chamber

(57) The invention relates to a cleaning method in which from a vacuum coating chamber (3) of a coating installation (1) for the coating of substrates (2) with alkali- or alkaline earth-metals, residues of alkali- or alkaline earth-metals are removed. For this purpose into the chamber (3) a gas from the group of N_2, O_2 or air is introduced, which reacts with the alkali- or alkaline earth-metals to form the corresponding solid compounds. Water can additionally be introduced into the vacuum coating chamber (3).

After the alkali- or alkaline earth-metals have reacted with the gas, the corresponding solid compound is removed from the vacuum coating chamber.

Fig. 1



Printed by Jouve, 75001 PARIS (FR)

Description

[0001] The invention relates to an arrangement and a method according to the preambles of claims 1 and 11.

[0002] Modem lithium batteries are, as a rule, produced in a vacuum chamber, wherein a substrate is provided with a lithium layer. The lithium layer is formed, for example, through the deposition on the substrate of lithium in the vapor state. Since lithium is highly reactive, contact by the operating personnel after opening the vacuum chamber must be avoided. Even if the excess lithium has been pumped out of the vacuum chamber, it is still possible for lithium particles deposited on the inner wall of the vacuum chamber or on facings and/or maskings to harm the operating personnel.

[0003] Methods for the production of lithium batteries are already known in which lithium is converted in a vacuum chamber into vapor, which is subsequently deposited on a substrate (JP 59-060866, JP 2003-007290, JP 2003-234100, JP 2007-207663).

Nothing is found in these publications regarding the cleaning of the vacuum chamber.

[0004] It is further known to eliminate undesirable depositions on the inside of a coating installation by means of a cleaning gas (JP 2003-229365). However, lithium or alkali metals are herein not listed.

[0005] Furthermore, cleaning a process chamber by means of a gas containing O_2 is known (US 2007/0163617 A1). Herein the cleaning is carried out at increased temperature and under vacuum. The gas preferably also contains H radicals, since the cleaning process can also be carried out by means of a plasma. However, the walls of the process chamber are cleaned of tungsten and not of lithium or another aggressive material.

[0006] A further method for cleaning coating chambers is disclosed in DE 103 38 275 A1. In this method the process chamber is flushed with a conditioned purge gas before a coating process. The purge gas is preferably comprised of O_2 and N_2 with a humidity value of maximally 30%. The coating chamber is cleaned before the coating process and the coating material is not lithium.

[0007] US 2002/0185067 A1 discloses a device and a method for the *in situ* cleaning of a throttle valve in a CVD system. Here a cleaning gas is introduced which can comprise F_2, C_2F_6, O_2 or NF_3. Lithium is not discussed.

[0008] A cleaning process for a coating chamber is furthermore known in which *inter* alia N_2 and O_2 are employed as cleaning gases (EP 1 612 857 A1). These gases are converted to plasma and subsequently serve for cleaning the inner wall of a CVD chamber. High frequency is utilized for the generation of the plasma. However, not Li, but rather Si_3N_4 or SiO_2 are removed.

[0009] EP 0 441 368 A discloses a device and a method for eliminating excess material from a PVD chamber. During a cleaning cycle a vacuum is generated in the PVD chamber and a gas mixture with reactive gas is introduced into the PVD chamber. The reactive gas is herein activated through plasma discharge. The objects of the cleaning are also screenings. The eliminated material is Ti, W or Al, not however Li.

[0010] The invention addresses the problem of cleaning such parts of a vacuum coating chamber which during the production of thin-film batteries are unintentionally coated, for example maskings, metal lining sheets and the like.

[0011] This problem is solved according to the characteristics of claims 1 and 11.

[0012] The advantage attained with the invention comprises in particular that unintentionally coated parts are cleaned in simple manner and the cycle times or service times are shortened. Since the cleaning can also be carried out cyclically, it is possible to operate a coating installation without interruption.

[0013] The invention consequently relates to a cleaning method in which from a vacuum coating chamber of a coating installation for the coating of substrates with alkali- or alkaline earth-metals, residues of alkali or alkaline earth-metals are removed. For this purpose into the chamber a gas from the group of N_2, O_2 or air is introduced which reacts with the alkali- or alkaline earth-metals to form the corresponding solid compounds. Water can still also be additionally introduced into the vacuum coating chamber.

After the alkali- or alkaline earth-metals have reacted with the gas, the corresponding solid compound is removed from the vacuum coating chamber.

[0014] An embodiment example of the invention is shown in the drawing and will be described in further detail in the following. In the drawing depict:

[0015] Fig. 1 a vacuum chamber for coating a substrate by means of a vaporized material.

[0016] A coating installation 1, in which a substrate 2 can be coated, is shown in Figure 1 in sectional view. This coating installation 1 includes a vacuum coating chamber 3, of which two side-walls 4, 5 are evident. Masking 6 is disposed between the substrate 2 and a vapor feed system 7, which comprises a vaporizer crucible 8, a valve 9 and a vapor inlet 10 to 13. The end of the vapor inlet is formed by a linear distributor 14 implemented as a vertically oriented tube with linearly disposed openings. These openings are located opposite the masking 6. By 15, 16 are denoted covers in the vacuum chamber 3.

[0017] In the vaporizer crucible 8 is melted, for example, lithium for the production of thin-film lithium batteries and vaporized. Instead of lithium, another reactive metal from the group of alkali- and alkaline earth-metals, for example cesium, could also be utilized.

[0018] The vaporized material arrives via the vapor inlet 10 to 13 at the distributor 14 and from here, via the masking

6, which does not need to be provided in every case, at the substrate 2. In addition, the vaporized material also reaches the covers 15, 16 and other parts which it is not intended to reach.

[0019] When the coating of substrate 2 is completed, the unintentionally coated parts must be freed of the coating in order for the operating personnel not to be harmed by the reactive lithium when opening the vacuum chamber 3 and removing the coated substrate 2.

[0020] However, in order for a person not to come into contact with the lithium or other alkaline earth- or alkali-metals, these metals must be removed from the installation. The removal of these reactive metals from the installation takes place after the coating process has been terminated and the substrates have been transferred from the coating installation 1 via a vacuum lock, not shown in Figure 1. After the substrates have been removed from the coating installation 1, one or several gases are introduced into the vacuum chamber 3 before the opening the vacuum chamber 3.

[0021] For this purpose, outside of vacuum chamber 3 several gas containers 20, 21, 22 are provided which contain the gases N_2, O_2 or air. Activation of the gases is not absolutely required. These gas tanks 20, 21, 22 are connected via supply pipes 23, 24, 25 and valves 26, 27, 28 with the vacuum chamber 3. If N_2 is introduced into the vacuum chamber 3, the N_2 molecules combine with lithium according to the equation $6\ Li + N_2 \rightarrow 2\ Li_3N$. This end product is a solid which falls from the vertical surfaces to the bottom of the vacuum chamber 3 or adheres at the site of the reaction.

[0022] If O_2 is introduced into the vacuum chamber 3, based on the expression $4\ Li + O_2$ the colourless powdery solid compound Li_2O is formed, which is also nontoxic and falls from vertical parts.

[0023] It is understood that instead of pure oxygen, air can also be introduced into the vacuum chamber 3. This air can herein be enriched with O_2. Since air contains both nitrogen as well as also oxygen, lithium consequently reacts with the nitrogen as well as also with the oxygen. It is here advantageous if the air has a certain humidity. To this end the air can additionally be enriched with water. If there is also water contained in the air, the following reaction takes place:

$$Li + H_2O \rightarrow LiOH + ½\ H_2.$$

[0024] When air and water are introduced, in addition to Li_3N and Li_2O, LiOH and Li_2CO_3 are also formed.
For instance, Li_2CO_3 is formed through the following reaction: $2\ LiOH + CO_2 \rightarrow Li_2CO_3 + H_2O$.
At high temperatures Li_2CO_3 breaks down again into Li_2O and CO_2. The same applies also to LiOH which breaks down into Li_2O and H_2O. The lithium compounds must in every case be nontoxic and remain stable in air.

[0025] Since the reactions of H_2O, O_2 and N_2 are exothermic, it is advantageous to cool the vacuum chamber 3. This can be carried out by means of a cooling system, not depicted in Figure 1.
In principle, the metal Li, or also the other alkali- and alkaline earth-metals, can be made to react with other substances, such as, for example, with halogens or hydrogen compounds of these halogens.
However, since these halogens or halogen compounds are highly reactive and can also chemically attack the chamber, it is necessary when employing these compounds to build the chamber of a material that is chemically inert relative to these compounds.

[0026] Although activation of the gases is not absolutely required, it is nevertheless advantageous to carry out the reaction at increased temperatures. A temperature in the range from 30° C up to 200° C can be selected, at which the reaction is started. It is obvious that at higher temperatures the reaction proceeds faster. It is of advantage if the reaction takes place at a pressure of up to 100 mbar. The choice of temperature as well as of pressure depends substantially on the design of the vacuum chamber 3. If only pure oxygen is utilized as the gas, the temperature can be, for example, 80° C and the pressure of the oxygen 100 mbar. This ensures optimal reaction conditions.
It is advantageous if during the cleaning process the reaction is monitored by means of a gas sensor 32. A gas sensor 32 to be considered is, for example, a mass spectrometer, a lambda probe or an IR or NIR spectrometer. Via these measuring devices the gas composition can be determined during the process. If a lambda probe is employed, oxygen is preferably added to the gas or gas mixture. In this case the oxygen content can be determined during the process. As long as there is still lithium in the chamber and reacts with the gases, the concentration of the reactive gases is below the concentration of the gases before their introduction into the vacuum chamber 3 vitiated with lithium. As soon as the lithium has reacted with the gases, the concentration of the gases reaches the starting value again. This indicates that the reaction process has been completed. The gas composition, which had been determined by means of the gas sensor 32, is supplied to an evaluation instrument 33. When the process is completed, by means of a pump 30 and an extraction fitting 31 the powder on the bottom of the vacuum chamber 3 can be suctioned out. It is also possible to vent the vacuum chamber 3 and subsequently to remove the powder by means of a dust extractor. It is herein advantageous to remove the lithium salt adhering on the walls of the vacuum chamber 3 by means of ultrasound such that it falls to the bottom. This facilitates the cleaning work considerably. By setting parameters such as, for example, pressure, temperature or the moisture content in the form of water in the gas or the gas mixture, the reaction with the lithium can be accelerated. In order to enrich gases with moisture, water is introduced into the vacuum chamber 3 via a feed pipe 35.

[0027] Whether the lithium salts remain adhered to the surface after the cleaning process or spall off and consequently fall to the bottom of the vacuum chamber 3 depends substantially on the layer thicknesses of the formed lithium salts.

If the lithium layers formed in the coating reaction are very thin, salts with a very small grain diameter are formed in the cleaning process. Such lithium layers remain preferably well adhered on the walls of the vacuum chamber 3. If during the coating process thick lithium layers have been formed on the walls of the vacuum chamber, layers are formed in the cleaning reaction with the gases, which layers are under mechanical stress, which can lead to the spalling of the coating. For this reason it can be advantageous to remove the salt residues still adhering on the walls of the vacuum chamber 3 by means of ultrasound.

Claims

1. Arrangement for removing alkali- or alkaline earth-metals from a vacuum coating chamber (3) of a coating installation (1) with at least one gas tank (20 - 22) connected via a supply pipe (23 - 25) with the vacuum coating chamber (3), which gas tank contains a gas from the group N_2, O_2 or air.

2. Arrangement as claimed in claim 1, **characterized In that** between the at least one gas tank (20 - 22) and the vacuum coating chamber (3) a valve (26 - 28) is provided.

3. Arrangement as claimed in claim 1, **characterized in that** the vacuum coating chamber (3) includes a feed pipe (35) for H_2O, via which H_2O can be introduced into the vacuum coating chamber (3).

4. Arrangement as claimed in claim 1, **characterized in that** the vacuum coating chamber (3) includes means with which the vacuum coating chamber (3) can be exposed to ultrasound.

5. Arrangement as claimed in claim 1, **characterized in that** the vacuum coating chamber (3) includes at least one gas sensor (32).

6. Arrangement as claimed in claim 5, **characterized in that** the gas sensor (32) is a mass spectrometer.

7. Arrangement as claimed in claim 5, **characterized In that** the gas sensor (32) is a lambda probe.

8. Arrangement as claimed in claim 1, **characterized in that** the vacuum coating chamber (3) includes at the bottom an extraction fitting (31) which is connected to a pump (30).

9. Arrangement as claimed in claim 5, **characterized in that** the gas sensor (32) is an IR or NIR spectroscope.

10. Arrangement as claimed in claim 1, **characterized in that** the metal is lithium.

11. Method for removing alkali- or alkaline earth-metals from a vacuum coating chamber (3) of a coating installation (1), **characterized by** the following steps:

    a) the vacuum coating chamber (3) is set under vacuum after the coating process has been completed,
    b) a gas from the group of N_2, O_2 or air is introduced into the vacuum coating chamber (3) such that the gas reacts with the alkali- or alkaline earth-metals in the vacuum coating chamber (3) and forms a solid compound,
    c) the solid compound is removed from the vacuum coating chamber (3).

12. Method as claimed in claim 11, **characterized in that** the metal is lithium.

13. Method as claimed in claim 11, **characterized in that** H_2O is additionally introduced into the vacuum coating chamber (3).

14. Method as claimed in claim 11, **characterized in that** the air is enriched with O_2.

15. Method as claimed in claim 11, **characterized in that** the gas content during the reaction is determined by means of a gas sensor (32).

16. Method as claimed in claim 15, **characterized in that** the gas content is determined by means of a mass spectrometer.

17. Method as claimed in claim 15, **characterized in that** the oxygen content is determined by means of a lambda probe.

18. Method as claimed in claim 11, **characterized in that** at the beginning of the process a temperature of 30° C up to 200° C is set.

19. Method as claimed in claim 18, **characterized In that** the temperature is 80° C.

20. Method as claimed in claim 11, **characterized In that** a pressure of 100 mbar is set.

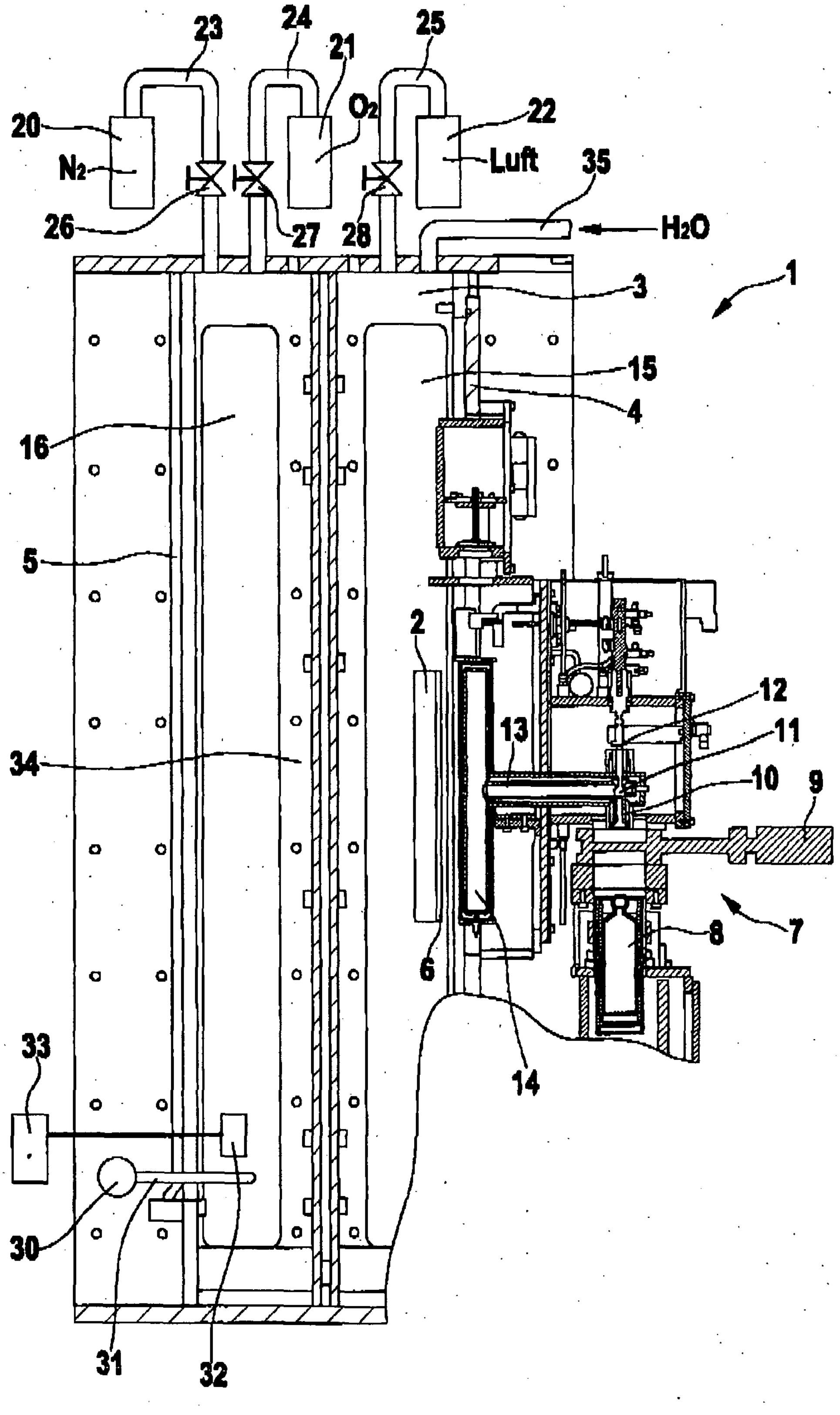
21. Method as claimed in claim 11, **characterized in that** the solid compound is removed from the vacuum coating chamber (3) by means of an extraction fitting (31) connected to a pump (30).

22. Method as claimed in claim 11, **characterized in that** the solid compound is removed from the vacuum coating chamber (3) by means of a dust extractor.

23. Method as claimed in claim 21 or 22, **characterized in that** the solid compound formed is detached by means of ultrasound from the walls of the vacuum coating chamber (3) before being removed from the vacuum coating chamber (3).

24. Method as claimed in claim 15, **characterized in that** the gas content is determined by means of an IR or NIR spectroscope.

Fig. 1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EUROPEAN SEARCH REPORT

Application Number
EP 08 00 9925

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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Munich	29 August 2008	Swiatek, Ryszard

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 08 00 9925

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