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KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

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(54) Title: LITHIUM-BASED SOLID STATE BATTERIES

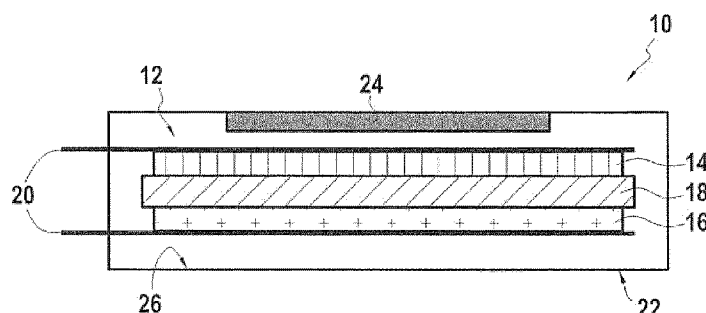


FIG.1

(57) Abstract: A lithium-based solid state battery (10) including a stack of cells (12), each cell (12) comprising a positive electrode (14), a negative electrode (16) and a solid electrolyte (18) disposed between the positive electrode (14) and the negative electrode (16), the lithium-based solid state battery (10) including a container (22), the stack of cells being enclosed in the container (22) and the lithium-based solid state battery (10) including sulfur (24) attached to the container (22).



LITHIUM-BASED SOLID STATE BATTERIESFIELD OF THE DISCLOSURE

5 [0001] The present disclosure is related to all-solid state batteries, lithium-based batteries or cells.

BACKGROUND OF THE DISCLOSURE

10 [0002] Lithium-based batteries are part of a family of rechargeable battery types in which lithium ions move from the negative electrode to the positive electrode during discharge and from the positive electrode to the negative electrode when charging.

[0003] There are various types of lithium-based batteries, and interest has
15 arisen in solid-state type batteries in recent years. In such batteries, an electrolyte of the battery, previously a liquid or gel, is replaced by a solid material. For example, JP 2011-028883 discloses a secondary battery with a lithium-ion-conductive nonaqueous electrolyte. Such solid state batteries tend to have improvements in performance as a temperature increases. Moreover,
20 these solid state batteries are safer as there is no liquid present in the batteries.

[0004] Nevertheless, abnormalities may occur during the use of the solid state battery that may produce temperature. The temperature may rise to a threshold temperature, which may result in battery damage and/or additional consequences. Devices intended to stop charging in case of over-charging of
25 the battery and/or when the temperature is too high are known.

SUMMARY OF THE DISCLOSURE

[0005] Currently, it remains desirable to increase the safety of lithium-based
30 solid state batteries. For example, the inventors of the present application have recognized that it is desirable to release the energy present in the solid state battery after charging has been stopped due to abnormal conditions.

[0006] Therefore, according to embodiments of the present disclosure, a lithium-based solid state battery is provided. The lithium-based solid state
35 battery includes a stack of cells, each cell including a positive electrode, a negative electrode and a solid electrolyte disposed between the positive electrode and the negative electrode, the lithium-based solid state battery

including a container, the stack of cells being enclosed in the container and the lithium-based solid state battery comprising sulfur attached to the container.

[0007] During a charging process of a lithium-based solid state battery, temperature may increase above a normal threshold. This increase in
5 temperature may result in battery damage and/or additional consequences. When the solid state battery is under abnormal conditions and the charging of the solid state battery is stopped, sulfur begins to sublime at 102°C. The gas sulfur may react with the lithium contained in the charged negative electrode of the lithium-based solid state battery to form lithium-sulfur compounds such as
10 Li_2S , Li_2S_2 , Li_2S_4 , Li_2S_6 , Li_2S_8 , thus discharging the negative electrode. The battery is therefore self-discharging. Moreover, these Li-S compounds are a high resistance layer, and it helps stopping the charging reaction. The lithium-based solid state battery is therefore safer compared to a solid state battery not having such sulfur in the container, even when the solid state battery is in an
15 abnormal configuration, during which the temperature of the solid state battery rises.

[0008] The sulfur may be attached to the container with a binder.

[0009] The sulfur is mixed with the binder, which helps attach the sulfur to the container.

20 [0010] The binder may be polyvinylidene fluoride.

[0011] The sulfur may be in a layer shape.

[0012] The sulfur may be applied by applying a slurry containing the sulfur onto the container.

[0013] The thickness of the layer of sulfur may be comprised between
25 0,001 mm and 10 mm, preferably between 0,01 mm and 1 mm.

[0014] The surface area of the layer of sulfur is comprised between 1 % and 100 % of the container inner surface, preferably between 10 % and 100 %.

[0015] It is intended that combinations of the above-described elements
30 and those within the specification may be made, except where otherwise contradictory.

[0016] It is to be understood that both the foregoing general description and the following detailed description are exemplary and explanatory only and are not restrictive of the disclosure, as claimed.

35 [0017] The accompanying drawings, which are incorporated in and constitute a part of this specification, illustrate embodiments of the disclosure and together with the description, serve to explain the principles thereof.

BRIEF DESCRIPTION OF THE DRAWINGS

[0018] Fig. 1 shows a schematic representation of an exemplary lithium-based battery with sulfur attached to the container according to a first embodiment;

[0019] Fig. 2 shows a schematic representation of an exemplary lithium-based battery with sulfur attached to the container according to a second embodiment.

DESCRIPTION OF THE EMBODIMENTS

[0020] Reference will now be made in detail to exemplary embodiments of the disclosure, examples of which are illustrated in the accompanying drawings. Wherever possible, the same reference numbers will be used throughout the drawings to refer to the same or like parts.

[0021] Fig. 1 shows a schematic representation of an exemplary lithium-based solid state battery 10. The lithium-based solid state battery 10 includes a stack of cells. For simplicity, one cell 12 has been represented in Fig. 1. Each cell 12 comprises a positive electrode 14, a negative electrode 16 and a solid electrolyte 18 disposed between the positive electrode 14 and the negative electrode 16. Each cell 12 also comprises two current collectors 20, the positive electrode 14, the solid electrolyte 18 and the negative electrode 16 being disposed between the two current collectors 20. When the lithium-based solid state battery 10 comprises a stack of cells 12, two adjacent cells 12 share a current collector 20.

[0022] The positive electrode 14 may comprise LiCoC_2 , LiMn_2O_4 , LiNiO_2 , $\text{LiCo}_w\text{Ni}_x\text{Mn}_y\text{Al}_z\text{O}_2$, LiFePO_4 , LiMnPO_4 , LiCoPO_4 or any suitable material for forming a positive electrode 14 in a lithium-based solid state battery 10. The negative electrode 16 may comprise C, Si, metallic Li, $\text{Li}_4\text{Ti}_5\text{O}_{12}$, TiO_2 , Sn, Al or any suitable material for forming a negative electrode 16 in a lithium-based solid state battery 10. The solid electrolyte 18 may comprise polymer ionic conductor such as polyethylene oxide (PEO)/ LiCF_3SO_3 , polyphenylene oxide (PPO)/ LiCF_3SO_3 , poly[ethylene oxide-co-2-(2-methoxyethoxy)ethyl glycidyl ether] (P(EO/MEEGE))/ LiCF_3SO_3 , polysiloxane/ LiClO_4 or inorganic ionic conductor such as $\text{Li}_2\text{S-SiS}_2$, $\text{Li}_{0.35}\text{La}_{0.55}\text{TiO}_3$ (LLTO), $\text{Li}_2\text{S-GeS}_2\text{-P}_2\text{S}_5$ or any suitable material for forming a solid electrolyte 18 in a lithium-based solid state

battery 10. The current collectors 20 may be made of stainless steel, gold (Au), platinum (Pt), nickel (Ni), aluminum (Al) or copper (Cu) or alloys comprising these materials. This list is not limitative. The two current collectors 20 may be made of the same material or the two current collectors may be made of different materials. For example, the current collector on the positive electrode side may be made of Al and the current collector on the negative electrode side may be made of Cu.

[0023] The lithium-based solid state battery 10 also includes a container 22 in which the stack of cells 12 is enclosed. The lithium-based solid state battery comprises sulfur 24 attached to the container 22, to an inner surface of the container 26.

[0024] In Fig. 1, the sulfur 24 is in a layer shape and there is one sulfur layer attached to the container 22. Typically, the layer of sulfur has a thickness comprised between 0,001 mm and 10 mm, preferably between 0,01 mm and 1 mm. For example, the layer of sulfur has a thickness equal to 0,01 mm. The thickness of the sulfur layer may be measured by scanning electron microscope and the thickness is measure in a direction perpendicular to the inner surface of the container 22.

[0025] The surface area of the sulfur may be comprised between 25 cm² and 1500 cm². It is comprised between 1 % and 100 % of the container inner surface, preferably between 10 % and 100 %.

[0026] In Fig. 2, there are two sulfur layer attached to the container 22 and the sulfur layer are disposed on different walls of the container.

[0027] The sulfur 24 may be attached to the container 22 by applying a slurry comprising sulfur and a binder to the container 22. The slurry is then dried at 80°C and thanks to the binder, is attached to the container 22.

[0028] For example, solvent for the slurry may be ethanol, toluene, heptane, xylene, dodecane, butanol, acetane, but are not limited to these solvents. Examples of binder may be polyvinylidene fluoride (PVDF), butadiene rubber (BR), styrene-butadiene rubber (SBR) or acrylate-butadiene rubber (ABR), but are not limited to these binders.

[0029] For example, the slurry may be obtained by mixing 40 mass% of sulfur with 55 mass% of solvent and 5 mass% of binder. The slurry may be prepared in a mortar and mixed for 15 minutes.

[0030] Particle size of the sulfur may be comprised between 0,1 µm (micrometre) to 10 µm.

[0031] In some embodiments, the sulfur 24 may be attached to the container 22 by melting solid sulfur. The solid sulfur is disposed at least on a part of the inner surface 26 of the container 22 and the sulfur is heated at 120°C for 10 minutes. The solid sulfur melts and, upon cooling, forms a layer of sulfur 24 on the container 22.

[0032] In some embodiments, the sulfur 24 may be attached to the container 22 by a vapour process, by depositing gaseous sulfur onto the inner surface 26 of the container 22.

[0033] For example, for a carbon negative electrode 16, the self-discharging reaction is as follows: $\text{LiC}_6 + \text{S} \rightarrow \text{LiS} + 6\text{C}$.

[0034] LiS in the above-equation could be anyone of the following Li-S compounds: Li_2S , Li_2S_2 , Li_2S_4 , Li_2S_6 , Li_2S_8 .

[0035] Throughout the description, including the claims, the term "comprising a" should be understood as being synonymous with "comprising at least one" unless otherwise stated. In addition, any range set forth in the description, including the claims should be understood as including its end value(s) unless otherwise stated. Specific values for described elements should be understood to be within accepted manufacturing or industry tolerances known to one of skill in the art, and any use of the terms "substantially" and/or "approximately" and/or "generally" should be understood to mean falling within such accepted tolerances.

[0036] Where any standards of national, international, or other standards body are referenced (e.g., ISO, etc.), such references are intended to refer to the standard as defined by the national or international standards body as of the priority date of the present specification. Any subsequent substantive changes to such standards are not intended to modify the scope and/or definitions of the present disclosure and/or claims.

[0037] Although the present disclosure herein has been described with reference to particular embodiments, it is to be understood that these embodiments are merely illustrative of the principles and applications of the present disclosure.

[0038] It is intended that the specification and examples be considered as exemplary only, with a true scope of the disclosure being indicated by the following claims.

CLAIMS

1. A lithium-based solid state battery (10) comprising a stack of cells (12), each cell (12) comprising a positive electrode (14), a negative electrode (16) and a solid electrolyte (18) disposed between the positive electrode (14) and the negative electrode (16), the lithium-based solid state battery (10) comprising a container (22), the stack of cells being enclosed in the container (22) and the lithium-based solid state battery (10) comprising sulfur (24) attached to the container (22).
2. The lithium-based solid state battery (10) according to claim 1, wherein the sulfur (24) is attached to the container with a binder.
3. The lithium-based solid state battery (10) according to claim 2, wherein the binder is polyvinylidene fluoride.
4. The lithium-based solid state battery (10) according to any of claims 1-3, wherein the sulfur (24) is in a layer shape.
5. The lithium-base solid state battery (10) according to claim 4, wherein the thickness of the layer of sulfur is comprised between 0,001 mm and 10 mm, preferably between 0,01 mm and 1 mm.
6. The lithium-base solid state battery (10) according to claim 4 or 5, wherein the surface area of the layer of sulfur is comprised between 1 % and 100 % of the container inner surface, preferably between 10 % and 100 %.

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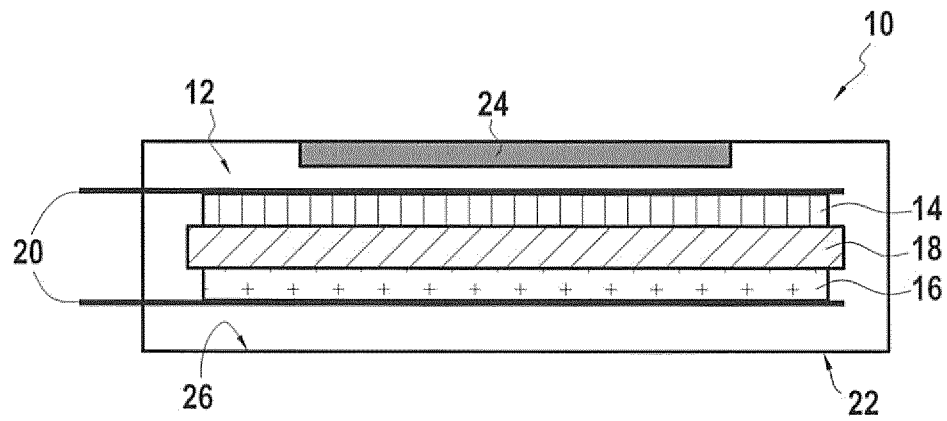


FIG.1

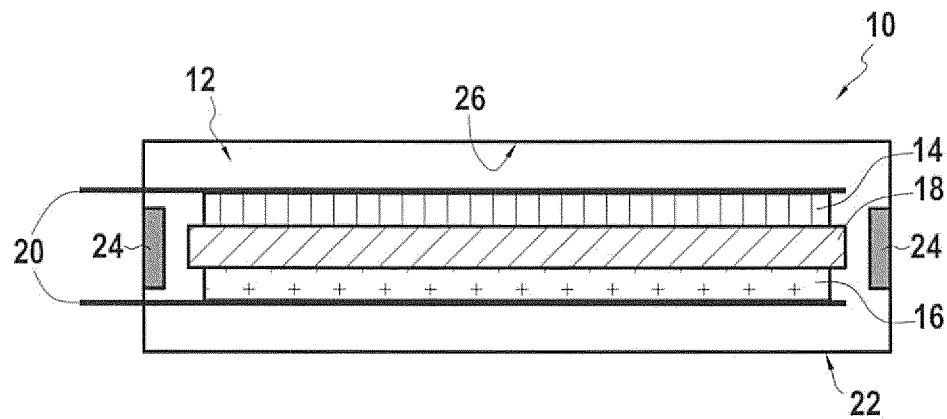


FIG.2

INTERNATIONAL SEARCH REPORT

International application No
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A. CLASSIFICATION OF SUBJECT MATTER INV. H01M4/38 H01M10/0562 H01M2/02 H01M10/052 H01M10/52 ADD. H01M10/42 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) H01M Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) EPO-Internal, WPI Data														
C. DOCUMENTS CONSIDERED TO BE RELEVANT <table border="1"> <thead> <tr> <th>Category*</th> <th>Citation of document, with indication, where appropriate, of the relevant passages</th> <th>Relevant to claim No.</th> </tr> </thead> <tbody> <tr> <td>X</td> <td>US 2010/239914 A1 (MIKHAYLIK YURIY V [US] ET AL) 23 September 2010 (2010-09-23) paragraphs [0006], [0043] - [0050], [0085], [0107]; figures 1,3 -----</td> <td>1</td> </tr> <tr> <td>A</td> <td>US 2011/129723 A1 (TSUCHIDA YASUSHI [JP]) 2 June 2011 (2011-06-02) paragraphs [0016], [0037] - [0040]; figure 1B -----</td> <td>1-6</td> </tr> <tr> <td>A</td> <td>JP 2008 103245 A (IDEMITSU KOSAN CO) 1 May 2008 (2008-05-01) page 1, line 2 - line 8 page 2, line 36 - line 41 page 3, line 13 - line 28; figures 1-4 ----- -/-</td> <td>1-6</td> </tr> </tbody> </table>			Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.	X	US 2010/239914 A1 (MIKHAYLIK YURIY V [US] ET AL) 23 September 2010 (2010-09-23) paragraphs [0006], [0043] - [0050], [0085], [0107]; figures 1,3 -----	1	A	US 2011/129723 A1 (TSUCHIDA YASUSHI [JP]) 2 June 2011 (2011-06-02) paragraphs [0016], [0037] - [0040]; figure 1B -----	1-6	A	JP 2008 103245 A (IDEMITSU KOSAN CO) 1 May 2008 (2008-05-01) page 1, line 2 - line 8 page 2, line 36 - line 41 page 3, line 13 - line 28; figures 1-4 ----- -/-	1-6
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.												
X	US 2010/239914 A1 (MIKHAYLIK YURIY V [US] ET AL) 23 September 2010 (2010-09-23) paragraphs [0006], [0043] - [0050], [0085], [0107]; figures 1,3 -----	1												
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Date of the actual completion of the international search 19 May 2017		Date of mailing of the international search report 01/06/2017												
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INTERNATIONAL SEARCH REPORT

International application No

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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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