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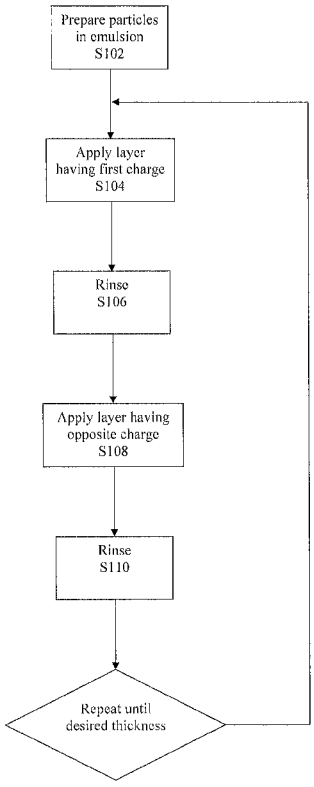
[Continued on next page]

(54) Title: CERAMIC COATING ON BATTERY SEPARATORS

FIG. 1



(57) Abstract: The present invention relates generally to electrochemical energy storage devices such as Li-ion batteries, and more particularly to a method of providing uniform ceramic coatings with controlled thicknesses for separators in such storage devices. Some embodiments of the invention utilize a layer by layer coating of nano/micro-sized particles dispersed in a solvent, which can be aqueous or non-aqueous. Other embodiments of the invention utilize a dry process such as PVD for depositing a ceramic film on a porous polyolefin separator. According to certain aspects of the invention, advantages of this approach include the ability to achieve a denser more uniform film with better controlled thickness with less waste and higher yield than current ceramic coating technology. An advantage of a ceramic coated separator is increased safety of cells.

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MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

— *with international search report (Art. 21(3))*

CERAMIC COATING ON BATTERY SEPARATORS

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] The present application claims priority to U.S. Prov. Appln. No. 61/736,968, the contents of which are incorporated by reference herein in their entirety.

FIELD OF THE INVENTION

[0002] The present invention relates generally to electrochemical energy storage devices such as Li-ion batteries, and more particularly to a method of providing uniform ceramic coatings with controlled thicknesses for separators in such storage devices.

BACKGROUND OF THE INVENTION

[0003] The current generation of Li-ion batteries use porous polyolefin separators which are susceptible to thermal shrinkage at elevated temperatures and may cause short between positive and negative electrodes or the corresponding current collectors. A ceramic coating on the separator helps to inhibit direct contact, but current methods for forming the coating using printing techniques and the like are unable to uniformly coat four microns or less of ceramic particles on battery separators.

SUMMARY OF THE INVENTION

[0004] The present invention relates generally to electrochemical energy storage devices such as Li-ion batteries, and more particularly to a method of providing uniform ceramic coatings with controlled thicknesses for separators in such storage devices. Some embodiments of the invention utilize a layer by layer coating of nano/micro-sized particles dispersed in a solvent, which can be aqueous or non-aqueous. Other embodiments of the invention utilize a dry process such as PVD for depositing a ceramic film on a porous polyolefin separator. According to certain aspects of the invention, advantages of this approach include the ability to achieve a denser more uniform film with better controlled thickness with less waste and higher yield than current ceramic coating technology. An advantage of a ceramic coated separator is increased safety of cells.

[0005] In accordance with these and other aspects, a method according to embodiments of the invention includes preparing a separator for an electrochemical storage

device; and using a controlled process to coat the separator with a ceramic layer having a desired thickness. In some embodiments, the controlled process comprises coating the separator with a first layer of ceramic particles having a first charge; coating the first layer with a second layer of ceramic particles having a second charge opposite the first charge; and repeating the coating steps until a ceramic coating having the desired thickness is obtained. In other embodiments, the controlled process comprises preparing a source material comprising a ceramic material; and depositing the ceramic layer on the separator in a PVD chamber until the desired thickness is obtained.

BRIEF DESCRIPTION OF THE DRAWINGS

[0006] These and other aspects and features of the present invention will become apparent to those ordinarily skilled in the art upon review of the following description of specific embodiments of the invention in conjunction with the accompanying figures, wherein:

[0007] FIG. 1 is a flowchart illustrating an example process for fabricating a ceramic coated separator according to embodiments of the invention;

[0008] FIG. 2 illustrates an example completed structure of a ceramic coated separator according to embodiments of the invention;

[0009] FIG. 3 is a flowchart illustrating another example process for fabricating a ceramic coated separator according to embodiments of the invention; and

[0010] FIG. 4 illustrates an example Li Ion battery structure having a ceramic coated separator according to embodiments of the invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0011] The present invention will now be described in detail with reference to the drawings, which are provided as illustrative examples of the invention so as to enable those skilled in the art to practice the invention. Notably, the figures and examples below are not meant to limit the scope of the present invention to a single embodiment, but other embodiments are possible by way of interchange of some or all of the described or illustrated elements. Moreover, where certain elements of the present invention can be partially or fully implemented using known components, only those portions of such known components that are necessary for an understanding of the present invention will be described, and detailed descriptions of other portions of such known components will be omitted so as not to obscure

the invention. Embodiments described as being implemented in software should not be limited thereto, but can include embodiments implemented in hardware, or combinations of software and hardware, and vice-versa, as will be apparent to those skilled in the art, unless otherwise specified herein. In the present specification, an embodiment showing a singular component should not be considered limiting; rather, the invention is intended to encompass other embodiments including a plurality of the same component, and vice-versa, unless explicitly stated otherwise herein. Moreover, applicants do not intend for any term in the specification or claims to be ascribed an uncommon or special meaning unless explicitly set forth as such. Further, the present invention encompasses present and future known equivalents to the known components referred to herein by way of illustration.

[0012] In general, the present inventors recognize that it would be advantageous to have the ability to achieve a denser more uniform film with better controlled thickness with less waste and higher yield than current ceramic coating technology. An advantage of having a ceramic coated separator in an electrochemical storage device such as a battery includes increased safety of cells.

[0013] In some embodiments, the invention includes a layer by layer coating of oppositely charged nano/micro-sized particles from an aqueous medium could be very suitable to forming a ceramic coating on separators such as porous polyolefin separators. An example methodology according to these embodiments of the invention is shown in FIG. 1.

[0014] In a first step S102, two suspensions or emulsions of oppositely charged particles are prepared. The ceramic particles may be an insulating oxide such as Al_2O_3, SiO_2, etc., or an ion conducting ceramic such as (Li,La)TiO_3, Li-La-Zr-O, sulfide based electrolytes, etc. The particles are preferably nanometer sized, but can be micrometer sized. The particles may be dense or hollow. One example of commercially available ceramic particles that can be used in embodiments of the invention are Al_2O_3, SiO_2 and MgO.

[0015] A charge may be imparted to the particles either by controlling the composition or pH of the solution or by attaching a charger polyelectrolyte to the particle, by adsorption or reactive chemical bonding (grafting). Polyelectrolytes are polymers whose repeating units bear an -ionizable group. These groups will dissociate in certain solutions (e.g. water), making the polymers charged. Polyelectrolyte properties are thus similar to both electrolytes (salts) and polymers (high molecular weight compounds), and are sometimes called polysalts. Some of the industrially used poly-electrolytes are polydiallyldimethylammonium chloride, poly(allylamine)-Nafion / poly(acrylic acid), linear

N, N-dodecyl,methyl-poly(ethyleneimine) / poly(acrylic acid), poly(ethyleneimine), poly(styrene sulfonate), poly(allylamine hydrochloride), poly(allylamine / poly(acrylic acid), poly(acrylic acid) / polyethylene oxide - block – polycaprolactone. Examples of negatively charged polyelectrolytes, when dissociated are poly(sodium styrene sulfonate) (PSS) and polyacrylic acid (PAA). Both PSS and PAA are negatively charged polyelectrolytes when dissociated. PSS is a 'strong' polyelectrolyte (fully charged in solution), whereas PAA is 'weak' (partially charged). Examples of positively charged polymers are Polyethylenimines, polylysene, Polyallylamine hydrochloride etc. Adsorption of polyelectrolytes on solid substrates is a surface phenomenon where long-chained polymer molecules with charged groups bind to a surface that is charged in the opposite polarity.

[0016] Although not shown as a separate step in FIG. 1, it may be necessary to prepare the separator if it is not inherently charged. In some embodiments, this preparation may include exposing the separator to a corona, chemically treating it (e.g. with an oxidizing agent), or adsorbing or grafting a polyelectrolyte to the surface of the separator. Having a charged separator is necessary for a first layer of oppositely charged particles to bind to the separator.

[0017] Step S104 includes applying a self-limiting layer consisting of one layer of particles. For example, if the separator is positively charged, then a negatively charged layer is applied. Once the surface is completely covered with the negatively charged layer, deposition of particles is ceased. It should be noted that the term "self-limiting" is used in this context to indicate that since a mono-layer of particles is deposited, there is no build-up of particles due to the natural repulsion between like charged particles. The application can be performed by coating the appropriate mixture onto the separator using a spray coating process, for example.

[0018] A rinsing process is performed in step S106 to rinse away any excess particles and solution. The rinsing may be performed by spraying water on the deposited layer or running the separator through a water bath. Alternatively, non-aqueous solvents such as acetonitrile, ethanol, N-Methyl-2-pyrrolidone, tetrahydrofuran etc. can be used. At this point, the separator is coated with one layer of ceramic particles having a thickness substantially corresponding to a diameter of the ceramic particles that have been used in the polymer solution.

[0019] In step S108 a second layer of particles of opposite charge to the previous layer is applied, and rinsing is performed in step S110. The application and rinsing can be

performed in the same manner as in steps S104 and S106. At this point, the separator will have a ceramic coating with a thickness substantially about twice the diameter of the ceramic particles being used.

[0020] Steps S104 to S110 are repeated as many times as necessary to achieve the desired thickness of the ceramic coating.

[0021] FIG. 2 illustrates a completed separator structure with one surface coated. Embodiments of the invention use existing battery separators and modify them with a ceramic particle coating using a method as described above. In embodiments, the separator is typically an approximately 25 micron thick structure made of polyolefin. Commercially available separators that are suitable for use in the invention include, for example, polymeric porous separators produced by Polypore (Celgard), Toray Tonen (Battery separator film (BSF)), SK Energy (lithium ion battery separator (LiBS), Evonik industries (SEPARION), Asahi Kasei (Hipore), DuPont (Energain), etc.

[0022] In the example shown in FIG. 2, a coating of about 3 microns thick has been applied on a surface of the separator that faces a negative electrode in a battery structure. However, both sides of the separator can be coated in some embodiments. In such embodiments, the entire coated separator structure can be about 16 microns thick, and perhaps as thin as 10 microns thick.

[0023] The above described embodiment is successful in achieving a denser and more uniform separator coating with better controlled thickness with less waste and higher yield than current ceramic coating technology. However, the inventors have discovered that it is not always possible to reliably form films using micro particles in the above process, as it is sometimes difficult to cause them to adhere to the surface. Using nano particles instead overcomes this problem, but it requires extra cycles of layer applications to achieve the desired film thickness.

[0024] Accordingly, alternative embodiments of the invention involve dry methodologies for forming the ceramic coating rather than the wet process described above. One example dry process involves the use of physical vapor deposition (PVD) techniques and does not require the use of particles. FIG. 3 is a flowchart illustrating an example process according to these embodiments of the invention.

[0025] As shown in FIG. 3, processing starts with preparing the film source material in step S302. This can include SiO_2 or Al_2O_3 in a solvent and preferably aqueous solvent with surfactant molecules to properly disperse the particles.

[0026] In step S304, the separator structure is placed in a PVD chamber such as Endura Impulsive PVD or Aristo tools from Applied Materials of Santa Clara, CA. The separator structure can include SiO_2, Al_2O_3, lithium conducting ceramic oxides such as doped variants of the garnet compositions, perovskites, anti-perovskites and lithium conducting sulfides, with a polymeric separator as substrate.

[0027] In step S306, processing continues until the desired thickness of material is deposited the coated separator is removed from the PVD chamber.

[0028] It should be noted that the steps S304 and S306 can be repeated for forming films on both sides of the separator structure.

[0029] The present inventors have noted certain advantages of the embodiment described above in connection with FIG. 3 over the previous embodiment. For example, the resulting coated structure has increased thermal stability and increased wettability. Moreover, the resulting coated structure has enhanced ion conductivity, which is believed to be caused by liquid-surface interaction between the SiO_2 or Al_2O_3 molecules into the pores of the separator material. This allows the entire separator structure to be reduced in thickness below 10 μm, with the film thicknesses on the order of nanometers.

[0030] FIG. 4 illustrates an example Li Ion battery structure having a coated separator according to any of the above embodiments of the present invention. A cross-sectional representation of an example of a Li Ion cell 400 is shown in FIG. 4, with a current collector 402, anode coating 404, a coated separator 408, a cathode coating 412 and a current collector 414. All components except collectors 402 and 414 also contain lithium ion electrolytes.

[0031] In embodiments of a Lithium Ion cell according to the invention, Lithium is contained in atomic layers of crystal structures of carbon graphite (LiC_6) at the anode and lithium manganese oxide ($LiMnO_4$) or lithium cobalt oxide (LiCoO) at the cathode. The other layers shown in Fig. 4 are needed to conduct electrons and positively charged Lithium Ions. The layers may be either coiled inside each other in a cylinder or pressed together in rectangular flat layers.

[0032] Current collector 402 can be a copper plate, while current collector 414 can be an aluminum plate. Electrolytes infused in 404, 408 and 412 can be comprised of a liquid/gel or a solid polymer and may be different in each. Coated separator 408 can be a separator as described in any of the embodiments above.

[0033] Although the present invention has been particularly described with reference to the preferred embodiments thereof, it should be readily apparent to those of ordinary skill

in the art that changes and modifications in the form and details may be made without departing from the spirit and scope of the invention. It is intended that the appended claims encompass such changes and modifications.

WHAT IS CLAIMED IS:

1. A method, comprising:

preparing a separator for an electrochemical storage device; and

using a controlled process to coat the separator with a ceramic layer having a desired thickness.

2. A method according to claim 1, wherein the controlled process comprises:

coating the separator with a first layer of ceramic particles having a first charge;

coating the first layer with a second layer of ceramic particles having a second charge opposite the first charge;

repeating the coating steps until a ceramic coating having the desired thickness is obtained.

3. A method according to claim 1, wherein the controlled process comprises:

preparing a source material comprising a ceramic material; and

depositing the ceramic layer on the separator in a PVD chamber until the desired thickness is obtained.

4. A method according to any of claims 1 or 2, wherein the ceramic particles comprise nano-particles.

5. A method according to any of claims 1 or 2, wherein the ceramic particles comprise micro-particles.

6. A method according to any of claims 1, 2 or 3, wherein the ceramic layer comprises one of Al_2O_3 and SiO_2.

7. A method according to any of claims 1, 2 or 3, wherein the ceramic layer comprises an ion conducting ceramic.

8. A method according to any of claims 1, 2 or 3, wherein the separator comprises porous polyolefin.

9. A method according to claim 2, further comprising imparting a charge to the ceramic particles by controlling a pH in a solution containing the ceramic particles.

10. A method according to claim 2, further comprising imparting a charge to the ceramic particles by attaching a charger polyelectrolyte to the ceramic particles.

11. A method according to any of claims 1, 2 or 3, wherein the desired thickness is less than 5 micrometers.

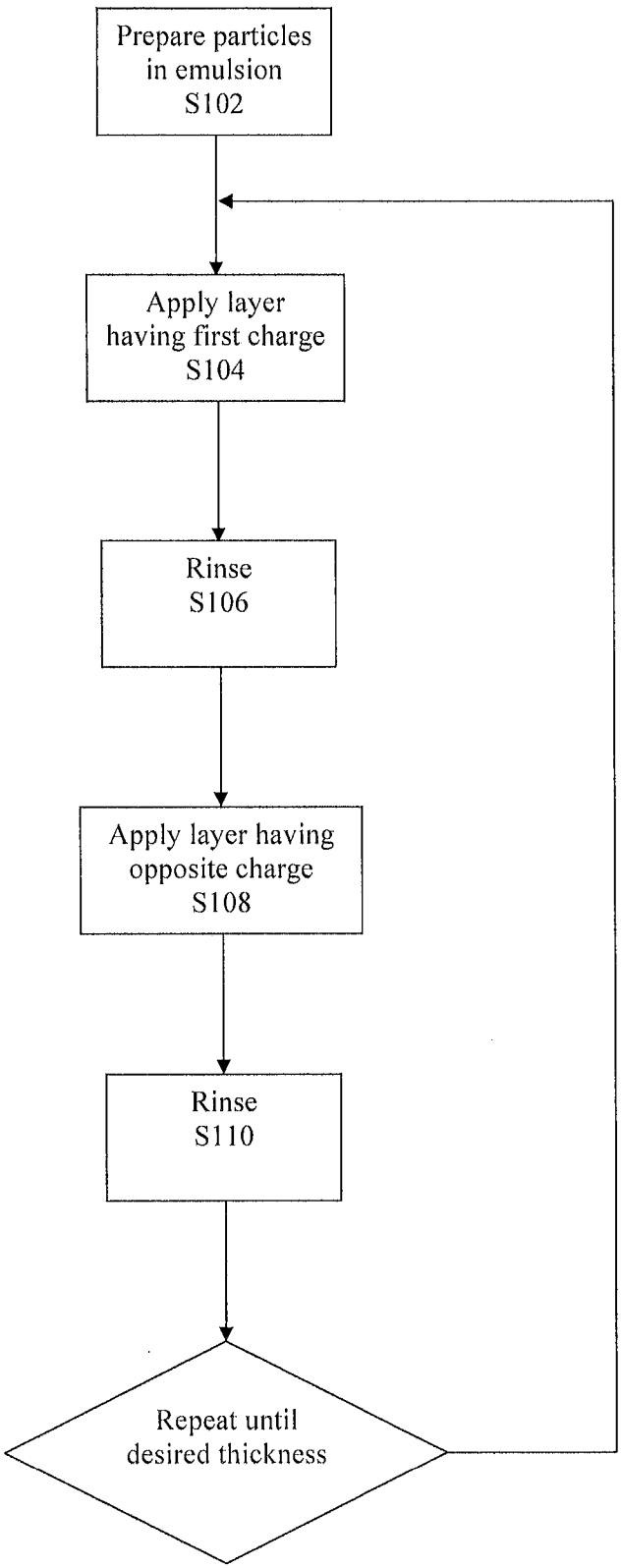
12. A method according to any of claims 1, 2 or 3, wherein the ceramic layer is formed on one of an anode facing side of the separator and a cathode facing side of the separator.

13. A method according to any of claims 1, 2 or 3, wherein the ceramic layer is formed on both of an anode facing side of the separator and a cathode facing side of the separator.

14. A separator having a coating as formed in any of claims 1 to 13.

15. A battery having a separator with a coating as formed in any of claims 1 to 13.

FIG. 1


Prepare particles in emulsion S102
Apply layer having first charge S104
Rinse S106
Apply layer having opposite charge S108
Rinse S110
Repeat until desired thickness

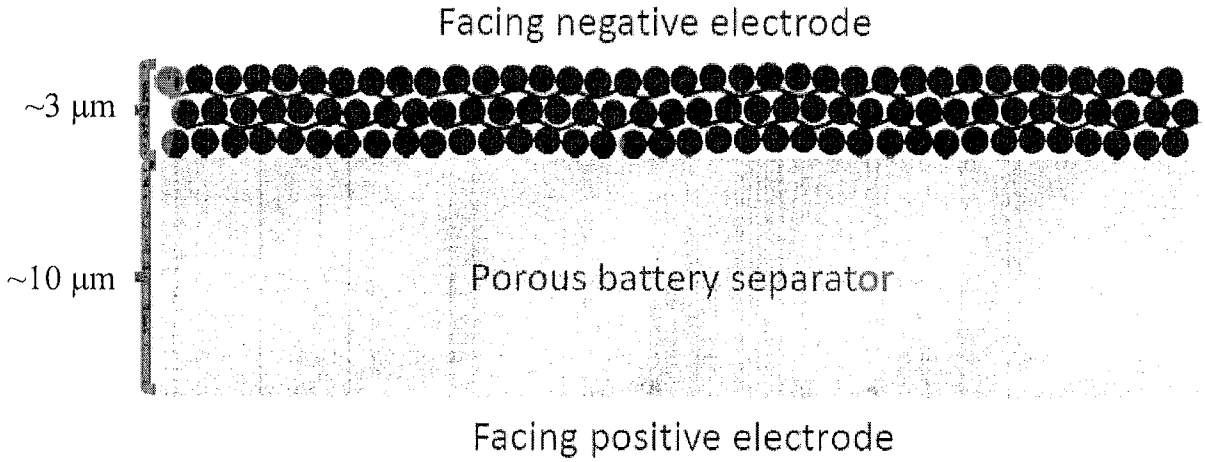

Facing negative electrode
~3 μm
~10 μm
Porous battery separator
Facing positive electrode

FIG. 2

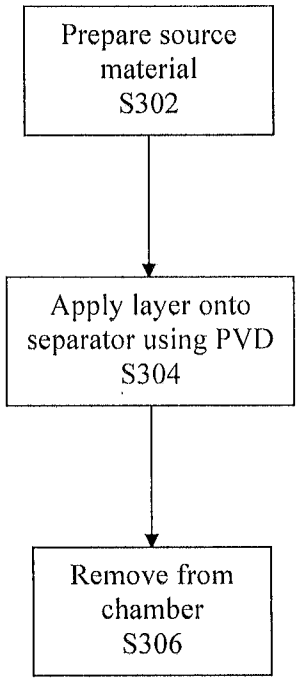

Prepare source material S302
Apply layer onto separator using PVD S304
Remove from chamber S306

FIG. 3

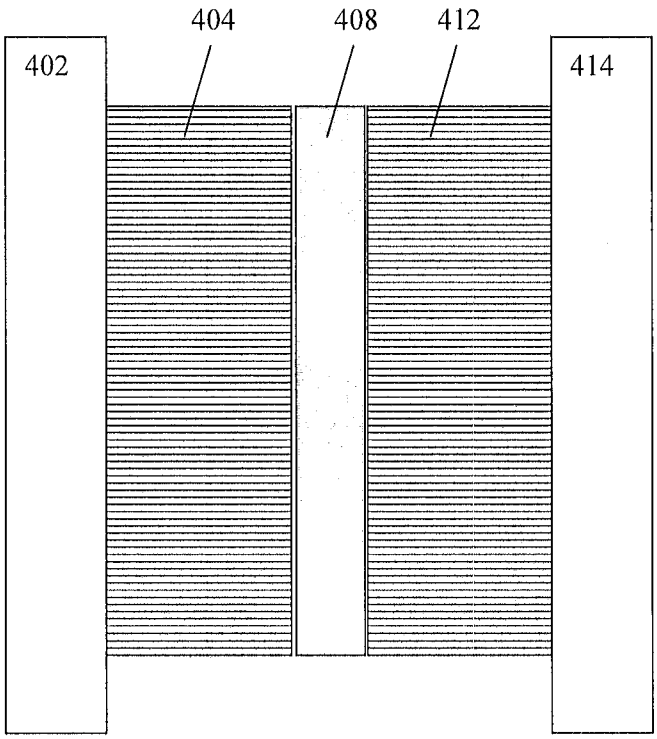


FIG. 4

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2013/074449

A. CLASSIFICATION OF SUBJECT MATTER

H01M 2/14(2006.01)i, H01M 2/16(2006.01)i

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 2/14; H01M 2/16; B05D 5/12; H01M 4/00; H01M 4/62; B05D 1/38; B05D 1/18

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Korean utility models and applications for utility models
Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
eKOMPASS(KIPO internal) & Keywords: separator, ceramic, coat, PVD, charge, impart, thickness, micro, nano

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2011-0200863 A1 (XINGEHENG XIAO et al.) 18 August 2011 See abstract, paragraphs [0014]-[0017], [0036], [0046], claims 1-8 and figures 1-3E.	1,3,6,8
Y		7,11-13
A		2,4,5,9,10
Y	US 2006-0166085 A1 (VOLKER HENNIGE et al.) 27 July 2006 See abstract, paragraphs [0038], [0119]-[0124] and claims 1-20.	7
Y	US 2011-0293990 A1 (JAE-YUL RYU et al.) 01 December 2011 See abstract, paragraphs [0029]-[0045], [0104] and claims 1-10.	11-13
A	US 2006-0078791 A1 (VOLKER HENNIGE et al.) 13 April 2006 See abstract, paragraphs [0136]-[0139], claims 1-20,26 and figures 1A-3B.	1-13
A	US 2011-0183203 A1 (CHUNSHENG DU et al.) 28 July 2011 See abstract, paragraphs [0052]-[0053], [0056], [0059], claims 1-5,12 and figures 14-15.	1-13

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents,such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
25 March 2014 (25.03.2014)	**25 March 2014 (25.03.2014)**

Name and mailing address of the ISA/KR
International Application Division
Korean Intellectual Property Office
189 Cheongsa-ro, Seo-gu, Daejeon Metropolitan City, 302-701, Republic of Korea
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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2013/074449

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☒ Claims Nos.: 14,15
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required addtional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of any additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
PCT/US2013/074449

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