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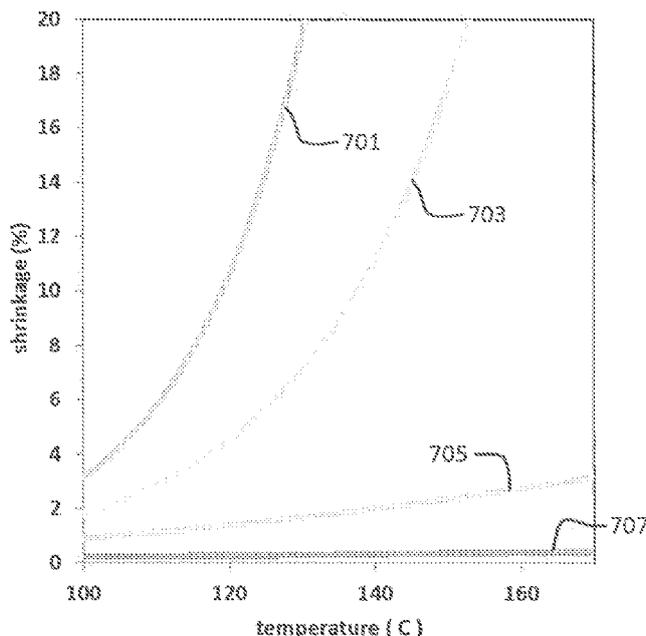
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(54) Title: NANOPOROUS COMPOSITE SEPARATORS WITH INCREASED THERMAL CONDUCTIVITY

Fig. 7



(57) Abstract: Nanoporous composite separators are disclosed for use in batteries and capacitors comprising a nanoporous inorganic material and an organic polymer material. The inorganic material may comprise Al<sub>2</sub>O<sub>3</sub>, AlO(OH) or boehmite, AlN, BN, SiN, ZnO, ZrO<sub>2</sub>, SiO<sub>2</sub>, or combinations thereof. The nanoporous composite separator may have a porosity of between 35-50% or between 40-45%. The average pore size of the nanoporous composite separator may be between 10-50 nm. The separator may be formed by coating a substrate with a dispersion including the inorganic material, organic material, and a solvent. Once dried, the coating may be removed from the substrate, thus forming the nanoporous composite separator. A nanoporous composite separator may provide thermal conductivity and dimensional stability at temperatures above 200°C.



## NANOPOROUS COMPOSITE SEPARATORS WITH INCREASED THERMAL CONDUCTIVITY

### 5 RELATED APPLICATIONS

[0001] This application claims benefit under 35 U.S.C. § 119(e) of U.S. Provisional Application No. 61/817,119, filed April 29, 2013 the content of which is incorporated by reference herein in its entirety.

### 10 FIELD OF THE DISCLOSURE

[0002] The present disclosure relates generally to the field of porous membranes and to electric current producing cells and separators for use in electric current producing cells. More particularly, this disclosure pertains to a porous separator membrane comprising an inorganic oxide or other inorganic material where the membrane has  
15 increased thermal conductivity compared to porous separator membranes consisting of polyolefin materials. Also, the present disclosure pertains to electric current producing cells, such as lithium ion cells and capacitors, comprising such porous separators with increased thermal conductivity.

### BACKGROUND OF THE DISCLOSURE

20 [0003] Lithium batteries, including rechargeable or secondary lithium ion batteries, non-rechargeable or primary lithium batteries, and other types such as lithium-sulfur batteries, are typically made by interleaving a plastic separator, a metal substrate with a cathode layer coated on both sides, another plastic separator, and another metal  
25 substrate with an anode layer coated on both sides. To maintain the alignment of the strips of these materials and for other quality reasons, this interleaving is usually done on automatic equipment, which is complex and expensive. Also, in order to achieve sufficient mechanical strength and integrity, the separators and the metal substrates are relatively thick, such as 10  $\mu\text{m}$  or more in thickness. For example, a typical  
30 thickness of the copper metal substrate for the anode coating layers is 10  $\mu\text{m}$ , a typical thickness of the aluminum metal substrate for the cathode coating layers is 12  $\mu\text{m}$ ,

and the plastic separators typically have thicknesses ranging from 12-20  $\mu\text{m}$ . These thick separators and metal substrates are not electrochemically active and thus lower the volume of the electroactive material in the electrodes of the lithium batteries. This limits the energy density and power density of the lithium batteries.

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#### SUMMARY OF THE DISCLOSURE

[0004] One aspect of the present disclosure pertains to a porous battery separator including ceramic particles and a polymeric binder, wherein the porous separator has a porosity between 35-50% and an average pore size between 10-50 nm. In some cases, the ceramic particles are selected from the group consisting of inorganic oxide particles and inorganic nitride particles. In some cases, the porous separator exhibits less than 1% shrinkage when exposed to a temperature of 200°C for at least one hour. In some cases, the ceramic particles include at least one of  $\text{Al}_2\text{O}_3$ ,  $\text{AlO}(\text{OH})$  or boehmite,  $\text{AlN}$ ,  $\text{BN}$ ,  $\text{SiN}$ ,  $\text{ZnO}$ ,  $\text{ZrO}_2$ ,  $\text{SiO}_2$ , and combinations thereof. In some cases, the ceramic particles include between 65-95% boehmite and a remainder of  $\text{BN}$ . In some cases, the ceramic particles include between 65-95% boehmite and a remainder of  $\text{AlN}$ . In some cases, the average pore size is between 10-90 nm. In some cases, less than 1% of the pores have a size outside of 10-90 nm. In some cases, the porosity is between 35-50%. In some cases, the polymeric binder includes a polymer selected from polyvinylidene difluoride (PVdF) and copolymers thereof, polyvinyl ethers, urethanes, acrylics, cellulose, styrene-butadiene copolymers, natural rubbers, chitosan, nitrile rubbers, silicone elastomers, PEO or PEO copolymers, polyphosphazenes, and combinations thereof. In some cases, the porous separator has a thermal conductivity that increases when temperature is raised from 25°C to 50°C and tested using one of ASTM E1461 and ASTM 1530. In some cases, the separator has a pore volume and greater than 90% of the pore volume includes pores having a pore diameter of less than 100 nm.

[0005] Another aspect of the present disclosure pertains to an electrochemical cell including an anode, a cathode, an inorganic electrolyte, comprising a lithium salt, and a porous separator layer including an organic polymer and a ceramic material, wherein the porous separator layer has a porosity between 35-50% and an average pore size between 10-90 nm and exhibits less than 1% shrinkage when exposed to a

temperature of 200°C for at least one hour. In some cases, the inorganic ceramic particles are selected from the group consisting of inorganic oxide particles and inorganic nitride particles. In some cases, the inorganic ceramic particles include Al<sub>2</sub>O<sub>3</sub>, AlO(OH) or boehmite, AlN, BN, SiN, ZnO, ZrO<sub>2</sub>, SiO<sub>2</sub>, and combinations thereof; and the organic polymer includes PVdF and copolymers thereof, polyvinyl ethers, urethanes, acrylics, cellulose, styrene-butadiene copolymers, natural rubbers, chitosan, nitrile rubbers, silicone elastomers, PEO or PEO copolymers, polyphosphazenes, and combinations thereof. In some cases, the average pore size is between 25-35 nm. In some cases, the porosity is between 40-45%.

10 [0006] Another aspect of the present disclosure pertains to a method of manufacturing a flexible porous composite separator. The method includes formulating a dispersion, wherein the dispersion includes an organic polymeric material, an inorganic ceramic material, and a solvent; applying the dispersion to a substrate to form a coating; drying and curing the coating; and removing the coating from the substrate thereby  
15 forming a flexible porous composite separator, wherein the porous separator has a porosity between 35-50% and an average pore size between 10-50 nm and exhibits less than 1% shrinkage when exposed to a temperature of 200°C for at least one hour. In some cases, the average pore size is between 20-40 nm and the porosity of the porous composite separator is between 40-45%. In some cases, the inorganic ceramic  
20 material includes at least one of boehmite, BN, and AlN.

[0007] Another aspect of the present disclosure pertains to a method of transferring heat through a battery including raising the temperature of an electrode in a lithium ion battery, and transferring heat from the electrode through a separator to a second electrode, the separator comprising porous ceramic particles and a polymer, wherein  
25 the separator has a porosity of 35-50% and an average pore size between 10-50 nm. In some cases, the average pore size is between 20-40 nm. In some cases, the separator has a plurality of pores and each of the pores has a diameter between 10-50 nm. In some cases, the separator has a plurality of pores and none of the pores has a diameter greater than 100 nm. In some cases, the separator has a porosity between  
30 40-45%. In some cases, the separator exhibits less than 1% shrinkage when exposed to a temperature of 200°C for at least one hour.

[0008] Another aspect of the present disclosure pertains to a flexible composite ceramic separator including a polymer; a first inorganic particulate material dispersed uniformly in the polymer; a second inorganic particulate material dispersed uniformly in the polymer, the second inorganic particulate material differing in either particle  
5 size or composition from the first inorganic particulate material; and wherein the flexible composite ceramic separator exhibits a thermal conductivity that is greater than the thermal conductivity of a comparative composite ceramic separator of the same composition that differs only in that it only includes a single inorganic  
10 particulate material at the same weight loading as the sum of the loadings of the first and second inorganic particulate materials. In some cases, the single inorganic particulate in the comparative composite ceramic separator is the same as one of the inorganic particulate materials of the flexible composite ceramic separator.

#### BRIEF DESCRIPTION OF THE FIGURES

[0009] For the purpose of illustrating the disclosure, particular experimental data are  
15 shown in the figures. It should be understood, however, that the disclosure is not limited to the precise data shown.

[0010] Figures 1-2 show thermograms of a polymeric separator and boehmite-based separator prepared according to an embodiment of the present disclosure.

[0011] Figure 3 shows a chart of the thermal conductivity (measured in W/m-K) of a  
20 polymeric separator compared to that of a nanoporous composite separator prepared according to an embodiment of the present disclosure.

[0012] Figure 4 shows a chart of the thermal conductivity (measured in W/m-K) of a  
25 polymeric separator material, a ceramic-coated polymeric separator material, and a nanoporous composite separator material prepared according to an embodiment of the present disclosure.

[0013] Figures 5-6 are graphs of the dimensional stability of various separator materials, including a nanoporous composite separator prepared according to an embodiment of the present disclosure.

[0014] Figures 7-8 are graphs of the dimensional stability of various separator materials, including a nanoporous composite separator prepared according to an embodiment of the present disclosure.

5 [0015] Figure 9 is a graph of the differential intrusion as a function of pore size diameter of a polymeric separator material and a nanoporous composite separator material prepared according to an embodiment of the present disclosure.

[0016] Figure 10 is a graph of the tensile stress as a function of percent extension of two separator materials, including a nanoporous composite separator material prepared according to an embodiment of the present disclosure.

10 [0017] Figure 11 is a graph of the particle size distribution of various boehmite and boron nitride (BN) blends, according to various embodiments of the present disclosure.

[0018] Figure 12 is a graph of the particle size distribution of various boehmite and alumina nitride (AlN) blends, according to various embodiments of the present  
15 disclosure.

[0019] Figure 13 is a graph of the viscosity profiles for various boehmite and BN blends, in liquid form, according to various embodiments of the present disclosure.

[0020] Figure 14 is a flow chart illustrating a method for preparing a nanoporous composite separator, according to an embodiment of the present invention

20 DETAILED DESCRIPTION OF THE DISCLOSURE

[0021] Nanoporous composite separators are disclosed comprising a composite of porous/nanoporous inorganic material and an organic polymer material. Such composite separators may be used, for instance, in batteries and/or capacitors. The inorganic material may comprise  $\text{Al}_2\text{O}_3$ ,  $\text{AlO}(\text{OH})$  or boehmite, AlN, BN, SiN, ZnO,  
25  $\text{ZrO}_2$ ,  $\text{SiO}_2$ , or combinations thereof. The organic polymer material may include, for example, polyvinylidene difluoride (PVdF) and/or copolymers thereof, polyvinyl ethers, urethanes, acrylics, cellulose, styrene-butadiene copolymers, natural rubbers, chitosan, nitrile rubbers, silicone elastomers, polyethylene oxide (PEO) or PEO copolymers, polyphosphazenes, or combinations thereof. In one embodiment, the

flexible nanoporous composite separator has a porosity between 35-50% or between 40-45% and an average pore size between 10-50 nm. The separator may be formed by coating a substrate with a dispersion including the inorganic material, organic material, and a solvent. Once dried, the coating may be removed from the substrate, thus forming the nanoporous composite separator. A nanoporous composite separator may provide thermal conductivity and dimensional stability at temperatures above 200°C.

### General Overview

[0022] The porous separator serves a key role in battery designs including prevention of physical contact between the anode and cathode, while facilitating ion transport for electrochemical energy supply as needed. Large format Li-ion batteries may operate in an average temperature range between 20-70°C; however, spikes in battery charge and/or discharge can push short term temperatures of such batteries beyond 110°C. Separators used for lithium ion batteries are typically polyolefin separators, such as polypropylene or polyethylene that may shrink and/or melt at such high temperatures due to, among other things, chemical breakdown. Although these plastic separators have the low electrical conductivity needed to insulate the electrodes of batteries from each other, plastic separators also have very low thermal conductivity and are therefore slow or inefficient in dissipating heat within a battery. As lithium ion batteries are increasingly utilized for higher capacity applications, such as for electric and/or hybrid vehicles, the need for improved safety is greatly increased because of the large size and high power rates of these batteries. In some cases, the battery separators may be required to maintain dimensional stability (i.e., < 5.0% shrinkage of the separator material) at temperatures at or above 200°C in order to ensure battery performance and safety. Coating of polyolefin separators with ceramic-based materials, and/or selecting higher melting polymer-based materials (PET, polyamides, PVdF, etc.) may increase the thermal stability/battery failure temperature somewhat; however, such techniques increase costs and fail to address a fundamental separator design issue: rapid, efficient, and uniform heat transfer throughout the cell.

[0023] Thus, in accordance with an embodiment of the present disclosure, nanoporous inorganic separator materials are disclosed which are electrically isolating, thermally conductive, and maintain dimensional stability at temperatures

above 200°C. In one embodiment, a nanoporous separator layer includes an inorganic material (also called ceramic and/or ceramic filler material) and an organic polymer which acts as a binder to hold the inorganic material together. This nanoporous composite separator exhibits a balance of mechanical strength, ionic conductivity, thermal conductivity, and electrical insulation rendering it suitable as a separator membrane for electrochemical cells. Suitable inorganic ceramic materials may include, for example, high thermal-conductivity ceramic particles such as Al<sub>2</sub>O<sub>3</sub>, AlO(OH) or boehmite, AlN, BN, SiN, ZnO, ZrO<sub>2</sub>, SiO<sub>2</sub>, and combinations of the above. A nanoporous composite separator may be formed, in some embodiments, by dispersing one or more of these inorganic materials with an organic or inorganic polymer material including, but not limited to: PVdF and/or copolymers thereof, polyvinyl ethers, urethanes, acrylics, cellulose, styrene-butadiene copolymers, natural rubbers, chitosan, nitrile rubbers, silicone elastomers, PEO or PEO copolymers, polyphosphazenes, and combinations of the above.

[0024] Table 1 provides a number of suitable example inorganic ceramic materials suitable for forming the nanoporous composite separator disclosed herein. The inorganic materials are listed along with their corresponding thermal and electrical properties.

<b>inorganic material</b>	<b>thermal conductivity (W/m-K)</b>	<b>volume resistivity (Ω-cm)</b>
h-BN	600/30*	>10 <sup>14</sup>
AlN	285	>10 <sup>14</sup>
Al <sub>2</sub> O <sub>3</sub>	30	>10 <sup>14</sup>
AlON	12.3	-
silica	1.3	>10 <sup>10</sup>
TiO <sub>2</sub>	11.7	~10 <sup>12</sup>
ZrO <sub>2</sub>	1.7	>10 <sup>10</sup>

Table 1

[0025] The thermal conductivity of hexagonal-Boron Nitride (h-BN) may be 600 or 30, in some embodiments, depending on its orientation. In addition to the inorganic materials shown in Table 1, the inorganic material may include boehmite, or a combination of any of these materials. Boehmite is a hydrated form of alumina that may be stable up to temperatures exceeding 600°C. The crystal structure of boehmite

is octahedral and is arranged in corrugated layers and is thus less prone to moisture pick-up than other aluminum based materials. In some embodiments, the various properties of the nanoporous composite separator may be tailored by adjusting, for example, particle size, organic polymer, particle size distribution, porosity of the inorganic material, specific surface area, and/or surface treatment of the nanoporous material. In some embodiments, the particle size distribution of the composite separator may be customized by blending boehmite with the various other inorganic materials in various proportions. For example, the nanoporous separator material may be pure boehmite (having less than 1% impurities), may be 90% boehmite and 10% BN or AlN, or it may be 70% boehmite and 30% BN or AlN. Various other proportions and combinations of these inorganic materials will be apparent, in light of this disclosure, and the present disclosure is not intended to be limited to any particular combination or proportion of inorganic materials. In some embodiments, the nanoporous composite separator includes inorganic particles and an organic polymeric to bond the inorganic particles together to form a homogeneous separator.

[0026] In one specific example embodiment, a nanoporous composite separator was prepared by mixing a 4:1 by weight blend of a boehmite pigment with a PVdF polymer and dispersants in an organic solvent blend comprising N-methylpyrrolidone (NMP) and 2-butanone and coating this mixture onto a silicone release film. In other embodiments, the solvent may comprise other suitable solvents or combinations of solvents such as, for example, benzene, ethyl benzene, toluene, xylene, MEK, NMP, or 2-butanone. Upon oven drying and subsequent delamination from the release substrate, a porous boehmite-based separator of 20  $\mu\text{m}$  in thickness was obtained. The porosity of this separator was about 42%, and the separator showed less than 1% shrinkage when heated in an oven at 220°C for 1 hour. In another embodiment, the nanoporous composite separator showed less than 0.5% shrinkage under similar heating conditions.

[0027] In another example embodiment, the organic polymer material may be a high molecular weight grade of PVdF, such as Solvay® Solef 5130 PVdF. This particular organic material can provide strong adhesion to current collectors, and in one specific example the nanoporous composite separator includes 4.5 parts boehmite to 1 part Solef 5130 by weight. In other embodiments, incorporation of a small amount of co-

monomer may enhance the cohesive strength of the separator material. In some embodiments, decreasing the ratio of inorganic oxide to organic polymer will lower the porosity and cycling rate capability of the separator material while increasing its mechanical strength.

5 [0028] In another example embodiment, the nanoporous composite separator may have a porosity between 35-50%, a uniform pore distribution over the entire separator material, and/or an average pore diameter of between 20-40 nm. In different sets of  
10 embodiments, the porosity of the separator is between 40-45%. In other sets of embodiments, the inorganic material may include no pores greater than 100 nm, 90 nm, 80 nm, 70 nm, 60 nm, 50 nm, or 40 nm. In still other sets of embodiments, less than 1% or less than 0.1% of the pores are greater than 100 nm, 90 nm, 80 nm, 70 nm, 60 nm, 50 nm, or 40 nm. In other sets of embodiments, the average pore size is  
15 between 10-50 nm, 20-40 nm, or 25-35 nm. In still other sets of embodiments, more than 99% or 99.9% of the pores of the composite separator are between 10-90 nm, 10-50 nm, 20-40 nm, or 25-35 nm. The nanoporous composite separator may exhibit similar properties in the machine direction (along the length of the sample) as in the transverse direction (along the width of the sample) if the separator material is not oriented during manufacturing.

[0029] In contrast to the cylindrical metal cells commonly used in lithium batteries  
20 for portable computers and other applications, many of the lithium batteries for vehicles are of a flat or prismatic design. In some cases, manufacturing high energy and economical lithium batteries for vehicles or other applications may involve increasing the proportion or percentage of the volume of the electroactive material in each battery and reducing the complexity and expense of the automated equipment to  
25 fabricate the battery. In some embodiments, a lithium battery may increase the content of electroactive material by implementing thinner separator and/or metal substrate layers. Such lithium batteries may be fabricated, for example, on less complex and less expensive automated processing equipment than, for example, the winding equipment utilized for portable computer batteries. In some embodiments,  
30 automated processing equipment may be particularly adapted for making flat or prismatic batteries.

[0030] In one embodiment, a dispersion may be prepared including the inorganic material, a polymer material, and a solvent in the desired proportions. The dispersion may then be coated on a temporary carrier substrate and allowed to dry and/or cure in order to obtain the desired mechanical properties prior to removal from the substrate.

5 Once dried and/or cured, the composite material may be removed from the substrate (or the substrate may be removed from the composite material), thus forming a nanoporous composite separator. In various embodiments, the porous separator layer may be a film with a thickness between 5-50  $\mu\text{m}$ , 10-30  $\mu\text{m}$ , 7-20  $\mu\text{m}$ , 10-20  $\mu\text{m}$ , or 2015-25  $\mu\text{m}$ .

### 10 Nanoporous Composite Separator Examples

[0031] Figures 1-2 show thermograms produced using an infrared camera (FLIR Model 8300) of a polymeric separator and boehmite-based separator prepared according to an embodiment of the present disclosure. Figure 1 is a thermogram of a polyethylene separator film upon exposure to a heated stainless steel substrate, while  
15 Figure 2 is a thermogram of a boehmite-based separator film of similar thickness exposed in like manner to the heated stainless steel substrate. The bright patches 101 in Figure 1 correspond to areas of increased heat concentration, while the darker patches 103 correspond to areas of decreased heat concentration. The uniform heat distribution observed in the boehmite-based separator of Figure 2 is evident compared  
20 to the uneven heat distribution seen with the plastic separator.

[0032] Figure 3 shows a chart of the thermal conductivity (measured in W/m-K) of a polymeric separator compared to that of a nanoporous composite separator prepared according to an embodiment of the present disclosure. The measurements in Figure 3 were done according to ASTM E1461 by the laser flash (transient) method using an  
25 LFA-447 from Netzsch® Instruments, Burlington, MA. These measurements illustrate the higher thermal conductivity of the nanoporous composite separator compared to a typical polyolefin separator material. Columns 301 and 303 chart the thermal conductivity of the nanoporous composite separator exposed to temperatures of 25°C and 50°C, respectively, while columns 305 and 307 chart the thermal  
30 conductivity of the polyolefin separator material exposed to 25°C and 50°C, respectively. In this particular embodiment, the polyolefin separator material used was 18  $\mu\text{m}$  thick Tonen® tri-layer, and the nanoporous composite separator was 21

μm thick and comprised a 4.5:1 ratio of Boehmite (Disperal® 10SR) to Solvay® Solef 5130. As can be seen in Figure 3, the thermal conductivity of the nanoporous composite separator is more than four times greater than that of the polyolefin separator of a similar thickness. This enhanced thermal conductivity is further  
5 increased, in some embodiments, when the temperature is increased from 25°C to 50°C. This property of increasing thermal conductivity as the temperature increases is particularly useful for safety in lithium ion batteries since they typically operate at temperatures around 50°C due to the heat generated during cell operation. It is  
10 important to rapidly and evenly distribute the heat throughout the cell to minimize the localized buildup of heat from any “hot spots” or other unevenly heated areas.

[0033] Figure 4 shows a chart of the thermal conductivity (measured in W/m-K) of a polymeric separator material, a ceramic-coated polymeric separator material, and a nanoporous composite separator prepared according to an embodiment of the present disclosure. The thermal conductivities charted in Figure 4 were measured according  
15 to the ASTM E1530 guarded hot plate (steady state) method with an estimated variation of ±3.0%. These measurements illustrate the higher thermal conductivity of the nanoporous composite separator compared to a typical polymeric separator material and a ceramic-coated polymeric separator material. The samples measured, in this particular example, include the two separator materials measured in Figure 3,  
20 as well as a third sample made from coating each side of the 18 μm thick Tonen® tri-layer with a 3.5 μm layer comprising a 5.5:1 ratio of boehmite to polymeric binder material. Columns 401 and 403 chart the thermal conductivity of the nanoporous composite separator measured at 25°C and 50°C, respectively; columns 405 and 407 chart the thermal conductivity of the polyolefin separator material measured at 25°C  
25 and 50°C, respectively; and columns 409 and 411 chart the thermal conductivity of the ceramic-coated polymeric separator material measured at 25°C and 50°C, respectively. In this particular embodiment, the thermal conductivity of the nanoporous composite separator is about twice that of the polyolefin separator material of a similar thickness, while the ceramic-coated separator material shows a  
30 slight improvement of about 20% in thermal conductivity over that of the polyolefin separator material.

[0034] Figures 5-6 are graphs of the dimensional stability of various separator materials, including a nanoporous composite separator prepared according to an embodiment of the present disclosure. Figure 5 graphs the dimensional change (measured in  $\mu\text{m}$ ) as a function of temperature of the various separator materials measured along the length of the samples, while Figure 6 graphs the dimensional change measured along the width of the material samples. In the example embodiments shown in Figures 5-6, 501 graphs the dimensional change of a polymeric separator material, 503 graphs the dimensional change of a one-side ceramic-coated polymeric separator material, 505 graphs the dimensional change of a two-side ceramic-coated polymeric separator material, and 507 graphs the dimensional change of a nanoporous composite separator prepared according to an embodiment of the present disclosure. In this particular example, the polymeric separator corresponding to graph 501 was a Tonen® tri-layer polyolefin with a thickness of 18  $\mu\text{m}$  and a Gurley air permeability of 300sec/100 cc. The separator corresponding to graph 503 was coated on a single side with a 3.5  $\mu\text{m}$  layer comprising a 5.5:1 ratio of Boehmite (Disperal® 10SR) to Arkema Kynar® 761, and the separator had a Gurley air permeability of 470 sec/100 cc. The separator corresponding to graph 505 was coated on two sides with a 3.5  $\mu\text{m}$  layer comprising a 5.5:1 ratio of Boehmite (Disperal® 10SR) to Arkema Kynar® 761, and the separator had a Gurley air permeability of 600 sec/100 cc. The nanoporous composite separator corresponding to graph 507 comprised a 4.5:1 ratio of Boehmite (Disperal® 10SR) to Solvay® Solef 5130, was 21  $\mu\text{m}$  thick, had a Gurley air permeability of 900 sec/100 cc, and a porosity of 40%. As seen in Figures 5-6, the dimensional stability of the polymeric separator 501 and the ceramic-coated polymeric separators 503-505 changes greatly between 100-170°C, while the nanoporous composite separator 507 maintains a high dimensional stability well beyond 200°C.

[0035] Figures 7-8 are graphs of the dimensional stability (measured as percent shrinkage) of various separator materials, including a nanoporous composite separator prepared according to an embodiment of the present disclosure. Figure 7 graphs the percent shrinkage as a function of temperature of the various separator materials measured along the length of the samples, while Figure 8 graphs the percent shrinkage measured along the width of the various material samples. The percent shrinkage graphed in Figures 7-8 was measured unrestrained over one hour according to the

ASTM 1204 standard test method for measuring linear dimensional changes. In the example embodiments shown, 701 graphs the percent shrinkage of a polymeric separator material, 703 graphs the percent shrinkage of a one-side ceramic-coated polymeric separator material, 705 graphs the percent shrinkage of a two-side ceramic-coated polymeric separator material, and 707 graphs the percent shrinkage of a nanoporous composite separator prepared according to an embodiment of the present disclosure. In this particular embodiment, the various separators corresponding to graphs 701, 703, 705, and 707 were the same separators described above in reference to graphs 501, 503, 505, and 507, respectively. As can be seen in Figures 7-8, the percent shrinkage of the polymeric separator material 701 and the first ceramic-coated polymeric separator 703 increases dramatically at temperatures above 100°C. The second ceramic-coated polymeric separator material 705 experiences a less dramatic increase in percent shrinkage, while the nanoporous composite separator material 707 maintains a low percent shrinkage at or below 0.5% at temperatures above 160°C.

[0036] Figure 9 is a graph of the log of the differential intrusion (measured as mL/g) as a function of pore size diameter (measured in  $\mu\text{m}$ ) of a polymeric separator material and a nanoporous flexible composite separator prepared according to an embodiment of the present disclosure. In this particular embodiment, 901 graphs the differential intrusion of a nanoporous composite separator 20  $\mu\text{m}$  thick, with a porosity of about 40%, and comprising a 4.5:1 ratio of boehmite (Disperal® 10SR) to Solvay® Solef 5130; and 903 graphs the differential intrusion of a 18  $\mu\text{m}$  thick Tonen® tri-layer polymeric separator material. As can be seen in this embodiment, the pore size distribution 901 corresponding to the nanoporous composite separator is concentrated at around 30 nm, and has a smaller mean size compared to the distribution 903 corresponding to the polymeric separator. In some embodiments, such a narrow pore size distribution and small average size may minimize the risk of dendritic penetration of the separator, which may cause localized short-circuits. In other embodiments, the pore size distribution of the nanoporous composite separator may be concentrated between 10-90 nm, 10-50 nm, 20-40 nm, or 25-35 nm. The pore size may be tailored, in some embodiments, through the formulation parameters of the nanoporous composite separator. As discussed above, decreasing the ratio of inorganic oxide to organic polymer will lower the porosity and cycling rate capability while increasing the mechanical strength of the material.

[0037] Figure 10 is a graph of the tensile stress (measured in psi) as a function of percent extension of two separator materials, including a nanoporous composite separator prepared according to an embodiment of the present disclosure. In this example embodiment, 1001 graphs the tensile stress of a 18  $\mu\text{m}$  thick Tonen® tri-layer polymeric separator material; while 1003 graphs the tensile stress of a nanoporous composite separator 20  $\mu\text{m}$  thick, with a porosity of about 40%, and comprising a 4.5:1 ratio of boehmite (Disperal® 10SR) to Solvay® Solef 5130. In this particular embodiment, the separators corresponding to graphs 1001, and 1003 were the same separators described above in reference to graphs 501, 503, 505, and 10 507, respectively. The U.S. Advanced Battery Consortium (USABC) target tensile stress is 1000 psi, and is shown by line 1005. The tensile stresses graphed in Figure 10 were measured along the length of the material samples using the ASTM D882-00 standard method for measuring the tensile properties of thin plastic sheeting. In another embodiment, the nanoporous composite separator 1003 has more than twice 15 the compression strength of the polymeric separator material 1001.

[0038] Figure 11 is a graph of the particle size distribution (volume percent as a function of particle size in  $\mu\text{m}$ ) of various boehmite and boron nitride (BN) blends, according to various embodiments of the present disclosure. In one specific example embodiment, the BN used is Saint-Gobain® Carbotherm PCTP05. As can be seen in 20 this example, 1101 plots the particle size distribution of a 100% boehmite material, 1103 plots the particle size distribution of a composition including 90% boehmite and 10% BN, and 1105 plots the particle size distribution of a composition including 70% boehmite and 30% BN, according to three embodiments of the present disclosure. The mode of the boehmite material distribution 1101 is at about 0.1  $\mu\text{m}$ . In this 25 particular example the boehmite material distribution 1101 includes a single mode, while the 90% boehmite composition 1103 and the 70% boehmite composition 1105 each display a bimodal distribution with modes at about 0.15–0.19  $\mu\text{m}$ , and at about 2–3  $\mu\text{m}$ .

[0039] Figure 12 is a graph of the particle size distribution (volume percent as a function of particle size in  $\mu\text{m}$ ) of various boehmite and alumina nitride (AlN) blends, according to various embodiments of the present disclosure. As can be seen in this 30 example, 1201 plots the particle size distribution of a separator material comprising

100% boehmite, 1203 plots the particle size distribution of a separator material comprising 90% boehmite and 10% AlN, and 1205 plots the particle size distribution of a separator material comprising 70% boehmite and 30% AlN, according to three embodiments of the present disclosure. In one embodiment, the mode of the boehmite material 1201 distribution is at about 0.1  $\mu\text{m}$ , similar to the mode of the boehmite material distribution 1101 graphed in Figure 11. In this particular example the boehmite material distribution 1201 includes a single mode, while the 90% boehmite material 1203 and the 70% boehmite material 1205 each display a bimodal distribution. The modes of the 90% boehmite material distribution 1203 are at about 0.15–0.19  $\mu\text{m}$ , and at about 8–11  $\mu\text{m}$ , while the modes of the 70% boehmite material distribution 1205 are at about 0.12–0.18  $\mu\text{m}$  and about 7–10  $\mu\text{m}$ .

[0040] In some embodiments, the inorganic particles may be of different sizes that are grouped around two, three or more modes. It is believed that by using a multi-modal distribution of particles of different sizes, the particles may be packed in a configuration in the separator that provides for increased heat transfer and better compression strength while maintaining or even improving porosity of the separator. The particles grouped around different modes may be of the same or different composition. For example, boehmite particles having a modal distribution centered at about 100 nm may be combined with additional boehmite particles having a modal distribution centered at about 2  $\mu\text{m}$ . In other embodiments, boehmite particles having a modal distribution centered at about 100 nm may be combined with AlN or BN particles having a modal distribution centered at about 2  $\mu\text{m}$ . The ratio of the particle size at a first mode to the particle size at a second mode can be, for example, greater than 1:2, 1:3, 1:5 or 1:10. In other embodiments, the ratio of the particle sizes of the two modes can be, for example, less than 1:100, 1:50, 1:20, 1:10, 1:5 or 1:3. The ratio (wt/wt) of the amounts of the two different sized particles used in a separator can be greater than 1:1, 2:1, 5:1 or 10:1.

[0041] Figure 13 is a graph of the viscosity profiles (measured as viscosity in cPs as a function of spindle speed in rpms) for the various boehmite and BN blends, in liquid form, according to various embodiments of the present disclosure. As can be seen in this example, 1301 plots the viscosity profile of a 100% boehmite material, 1303 plots the viscosity profile of a composition including 90% boehmite and 10% BN, and 1305

plots the viscosity profile of a composition including 70% boehmite and 30% BN, according to three embodiments of the present disclosure.

[0042] In some embodiments, the BN-modified compositions 1103-1105 and 1303-1305 may have higher thermal conductivities than a pure boehmite composition due to a dense packing of the blended filler that is enabled by the bimodal particle size distribution. Likewise, in other embodiments the AlN-modified compositions 1203-1205 may have higher thermal conductivities than a pure boehmite composition due to the bimodal particle size distribution of the AlN-modified composition.

[0043] Figure 14 is a flow chart illustrating a method for preparing a nanoporous composite separator, according to an embodiment of the present invention. The method may begin by mixing 1401 inorganic particles with a solvent. In some embodiments, the inorganic particles may include  $Al_2O_3$ ,  $AlO(OH)$  or boehmite, AlN, BN, SiN, ZnO,  $ZrO_2$ ,  $SiO_2$ , or combinations thereof, and the solvent may include toluene, xylene, MEK, NMP, 2-butanone, or any other suitable solvent or combinations thereof. The method may continue with adding 1402 the polymeric binder material in order to form a dispersion. In some embodiments, the polymeric binder material may include polyvinylidene difluoride (PVdF) and copolymers thereof, polyvinyl ethers, urethanes, acrylics, cellulose, styrene-butadiene copolymers, natural rubbers, chitosan, nitrile rubbers, silicone elastomers, PEO or PEO copolymers, polyphosphazenes, or combinations thereof. The method may continue with coating 1403 the dispersion onto a substrate and drying/curing 1404 the dispersion, thus forming the nanoporous composite separator. Once dried, the method may continue with removing 1405 the nanoporous composite separator from the substrate.

[0044] While the disclosure has been described in detail and with reference to specific and general embodiments thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from the spirit and scope thereof.

CLAIMS

What is claimed:

1. A porous battery separator comprising:  
ceramic particles; and  
5 a polymeric binder, wherein the porous separator has a porosity between 35-50% and an average pore size between 10-50 nm.
2. The porous separator of claim 1, wherein the porous separator exhibits less than 1% shrinkage when exposed to a temperature of 200°C for at least one hour.
- 10 3. The porous separator of claim 1 or 2, wherein the ceramic particles are selected from the group consisting of inorganic oxide particles and inorganic nitride particles.
4. The porous separator of any of claims 1-3, wherein the ceramic particles comprise at least one of Al<sub>2</sub>O<sub>3</sub>, AlO(OH) or boehmite, AlN, BN, SiN, ZnO,  
15 ZrO<sub>2</sub>, SiO<sub>2</sub>, and combinations thereof.
5. The porous separator of any of claims 1-4, wherein the ceramic particles comprise between 65-95% boehmite and a remainder of BN.
6. The porous separator of any of claims 1-4, wherein the ceramic particles comprise between 65-95% boehmite and a remainder of AlN.
- 20 7. The porous separator of claim 1, wherein the average pore size is between 10-90 nm.
8. The porous separator of claim 1, wherein less than 1% of the pores have a size outside of 10-90 nm.
9. The porous separator of claim 1 wherein the porosity is between 35-  
25 50%.
10. The porous separator of claim 1, wherein the polymeric binder comprises a polymer selected from a polyvinylidene difluoride (PVdF) and copolymers thereof, polyvinyl ethers, urethanes, acrylics, cellulose, styrene-

butadiene copolymers, natural rubbers, chitosan, nitrile rubbers, silicone elastomers, PEO or PEO copolymers, polyphosphazenes, and combinations thereof.

11. The porous separator of claim 1, wherein the porous separator has a thermal conductivity that increases when temperature is raised from 25°C to 50°C and  
5 tested using one of ASTM E1461 and ASTM 1530.

12. The porous separator of claim 1, wherein the separator has a pore volume and greater than 90% of the pore volume comprises pores having a pore diameter of less than 100 nm.

13. An electrochemical cell comprising:  
10 an anode;  
a cathode;  
an inorganic electrolyte comprising a lithium salt; and  
a porous separator layer comprising an organic polymer and a ceramic material, wherein the porous separator layer has a porosity between 35-50%  
15 and an average pore size between 10-90 nm and exhibits less than 1% shrinkage when exposed to a temperature of 200°C for at least one hour.

14. The electrochemical cell of claim 13, wherein the inorganic ceramic particles are selected from the group consisting of inorganic oxide particles and inorganic nitride particles.

20 15. The electrochemical cell of claim 14, wherein the ceramic material comprises Al<sub>2</sub>O<sub>3</sub>, AlO(OH) or boehmite, AlN, BN, SiN, ZnO, ZrO<sub>2</sub>, SiO<sub>2</sub>, and combinations thereof; and wherein the organic polymer comprises PVdF and copolymers thereof, polyvinyl ethers, urethanes, acrylics, cellulose, styrene-butadiene copolymers, natural rubbers, chitosan, nitrile rubbers, silicone elastomers,  
25 PEO or PEO copolymers, polyphosphazenes, and combinations thereof.

16. The electrochemical cell of claim 13, wherein the average pore size is 25-35 nm.

17. The electrochemical cell of claim 13, wherein the porosity is 40-45%.

18. A method of manufacturing a flexible porous composite separator comprising:
- formulating a dispersion, wherein the dispersion comprises an organic polymeric material, an inorganic ceramic material, and a solvent;
- 5 applying the dispersion to a substrate to form a coating;
- drying and curing the coating; and
- removing the coating from the substrate thereby forming a flexible porous composite separator, wherein the porous separator has a porosity between 35-50% and an average pore size between 10-50 nm and exhibits less than 1% shrinkage when exposed to a temperature of
- 10 200°C for at least one hour.
19. The method of claim 18, wherein the average pore size is between 20-40 nm and the porosity of the porous composite separator is between 40-45%.
20. The method of claim 18, wherein the inorganic ceramic material
- 15 comprises at least one of boehmite, BN, and AlN.
21. A method of transferring heat through a battery, the method comprising:
- raising the temperature of an electrode in a lithium ion battery; and
- transferring heat from the electrode through a separator to a second electrode,
- 20 the separator comprising porous ceramic particles and a polymer, wherein the separator has a porosity of 35-50% and an average pore size between 10-50 nm.
22. The method of claim 21, wherein the average pore size is between 20-40 nm.
- 25 23. The method of claim 21, wherein the separator has a plurality of pores and each of the pores has a diameter between 10-50 nm.
24. The method of claim 21, wherein the separator has a plurality of pores and fewer than 1% or 0.1% of the pores have a diameter greater than 100 nm.

25. The method of claim 21, wherein the separator has a porosity between 40-45%.

26. The method of claim 21, wherein the separator exhibits less than 1% shrinkage when exposed to a temperature of 200°C for at least one hour.

5 27. A flexible composite ceramic separator comprising:  
a polymer;  
a first inorganic particulate material dispersed uniformly in the  
polymer;  
10 a second inorganic particulate material dispersed uniformly in the  
polymer, the second inorganic particulate material differing in either particle  
size or composition from the first inorganic particulate material; and  
wherein the flexible composite ceramic separator exhibits a thermal  
conductivity that is greater than the thermal conductivity of a comparative  
15 composite ceramic separator of the same composition that differs only in that  
it only includes a single inorganic particulate material at the same weight  
loading as the sum of the loadings of the first and second inorganic particulate  
materials.

20 28. The flexible composite ceramic separator of claim 27, wherein the  
single inorganic particulate in the comparative composite ceramic separator is the  
same as one of the inorganic particulate materials of the flexible composite ceramic  
separator.

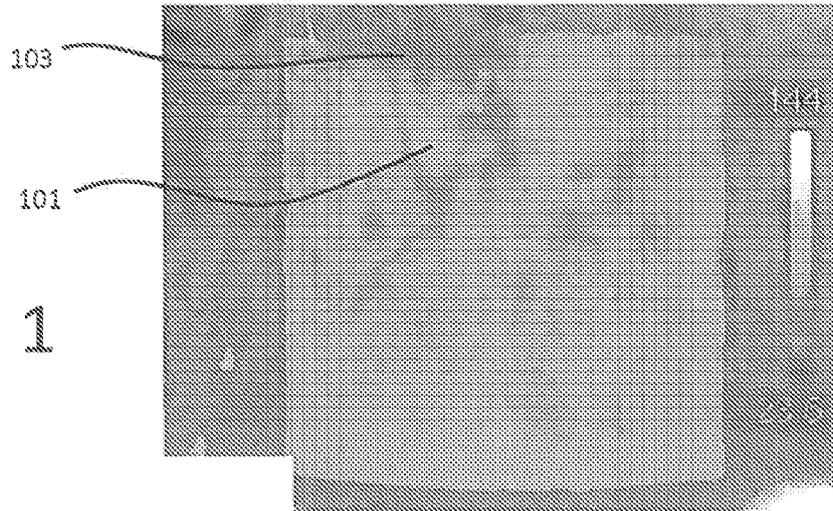


Fig. 1

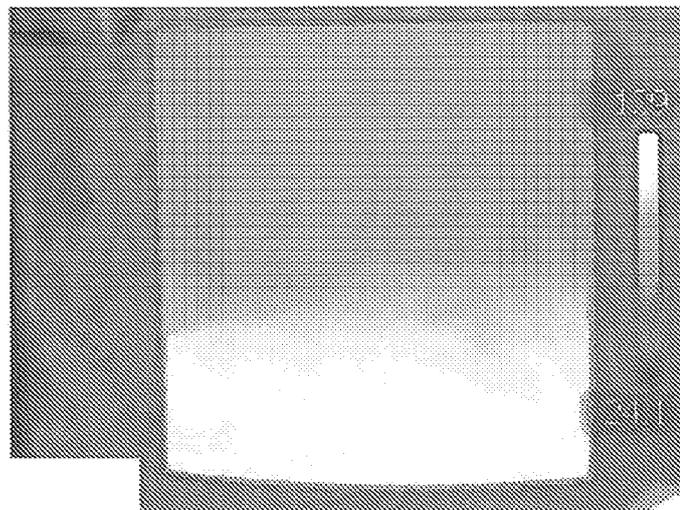


Fig. 2

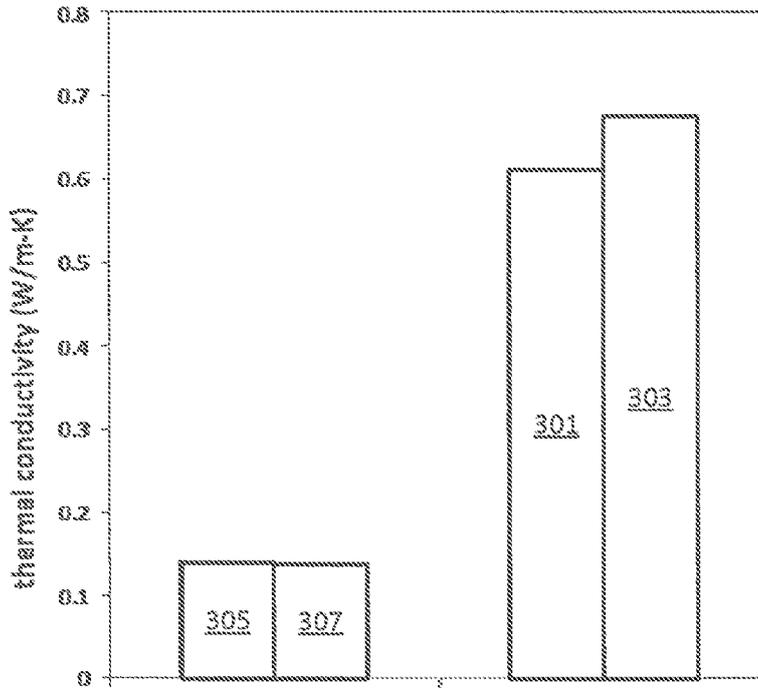


Fig. 3

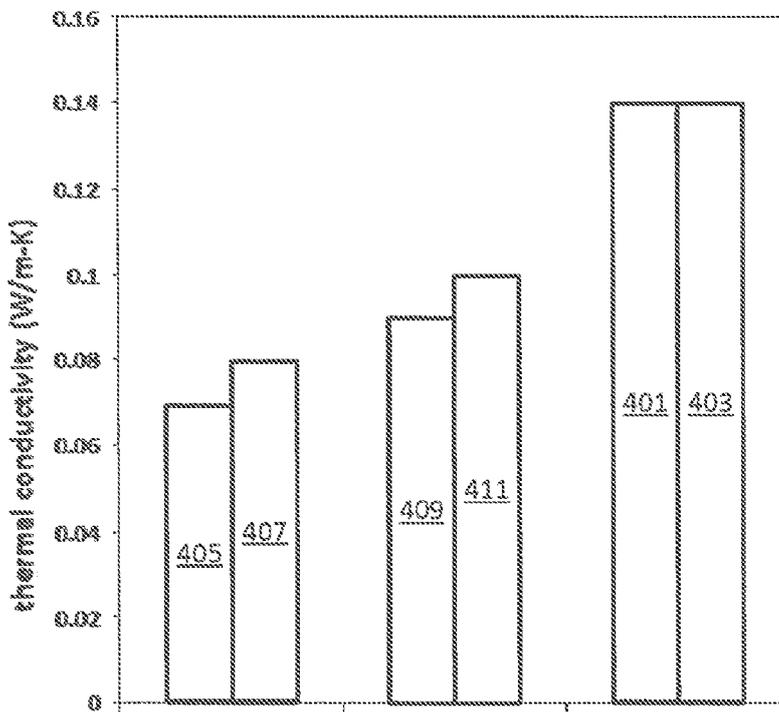


Fig. 4

Fig. 5

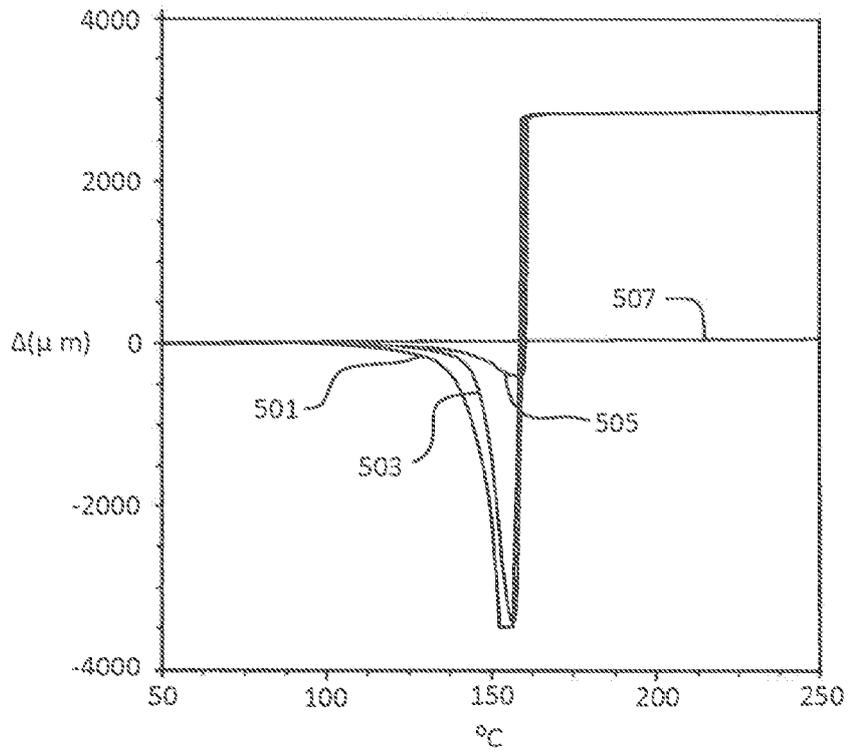


Fig. 6

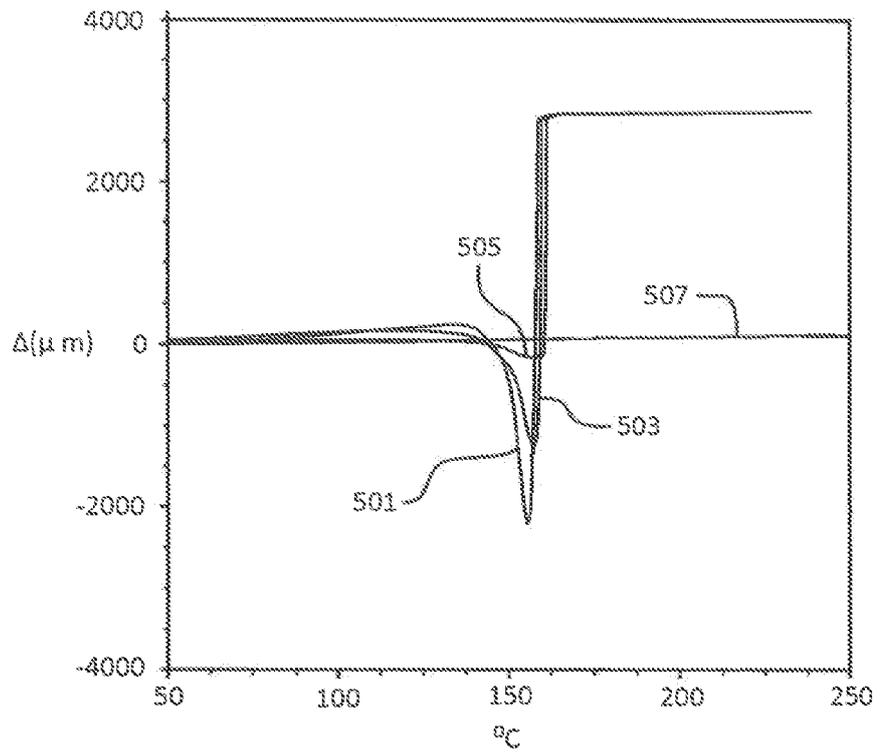


Fig. 7

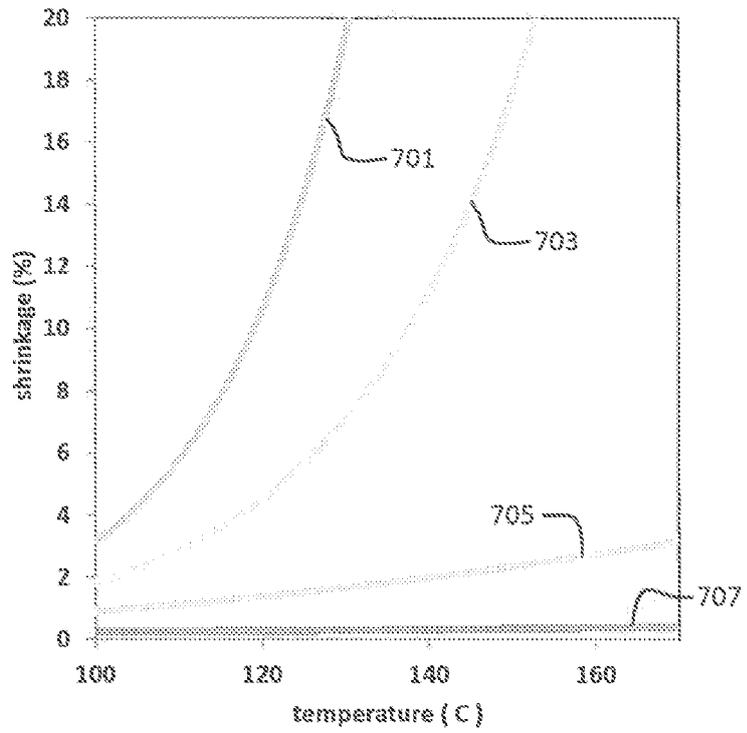
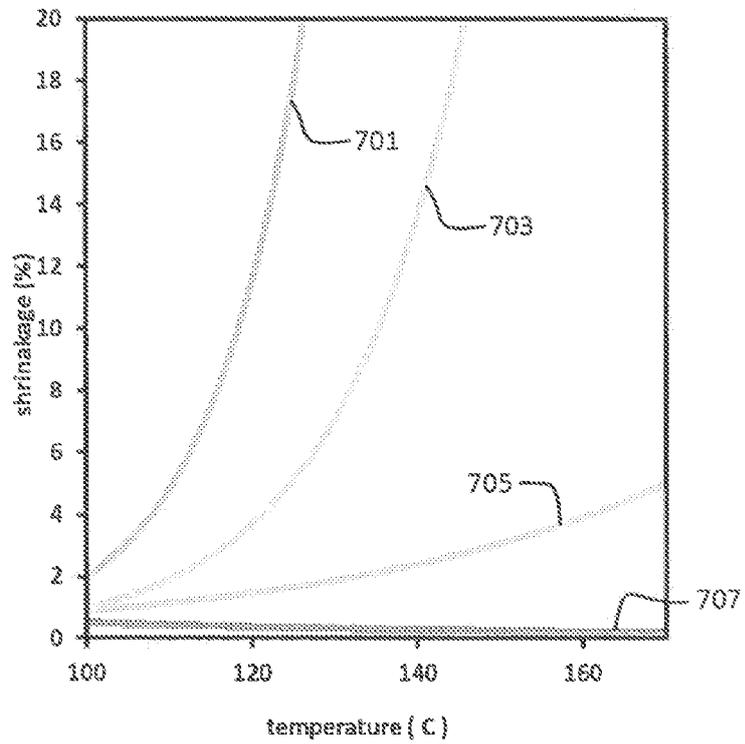


Fig. 8



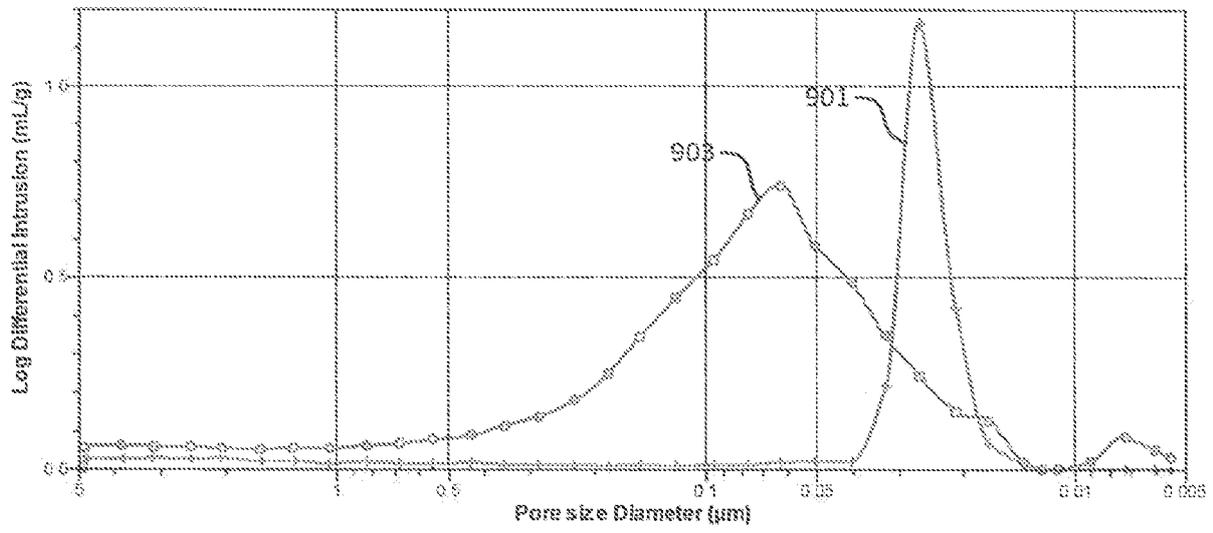


Fig. 9

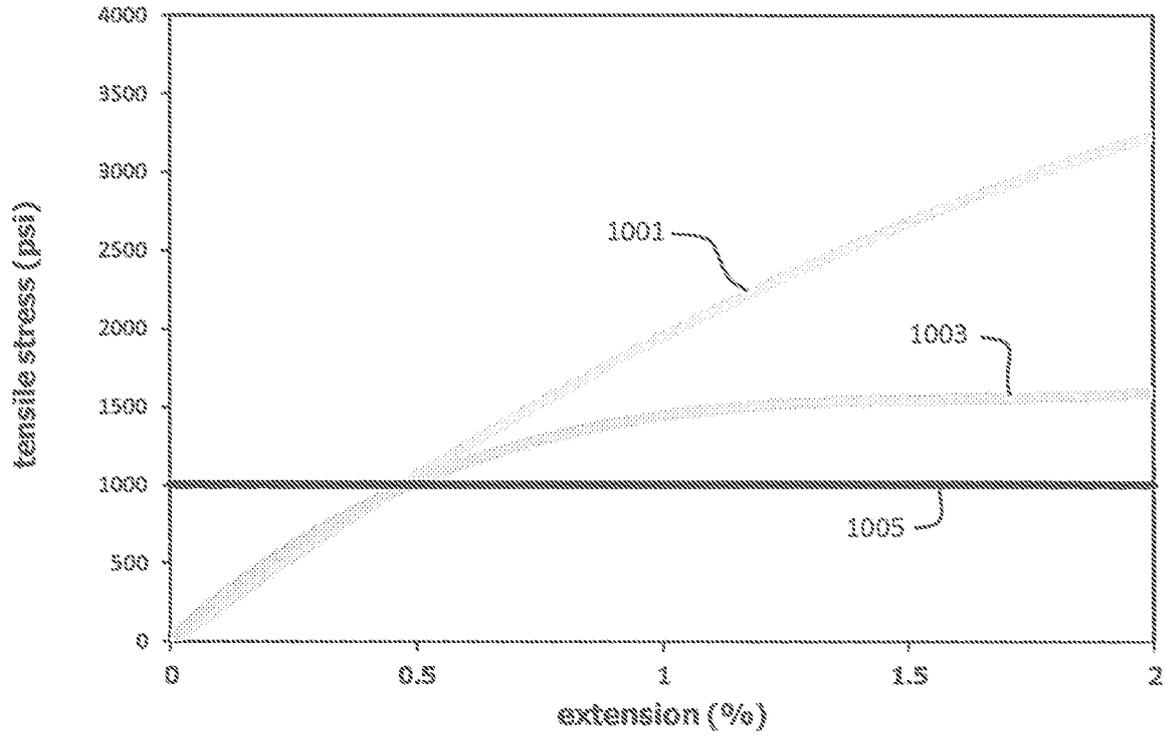


Fig. 10

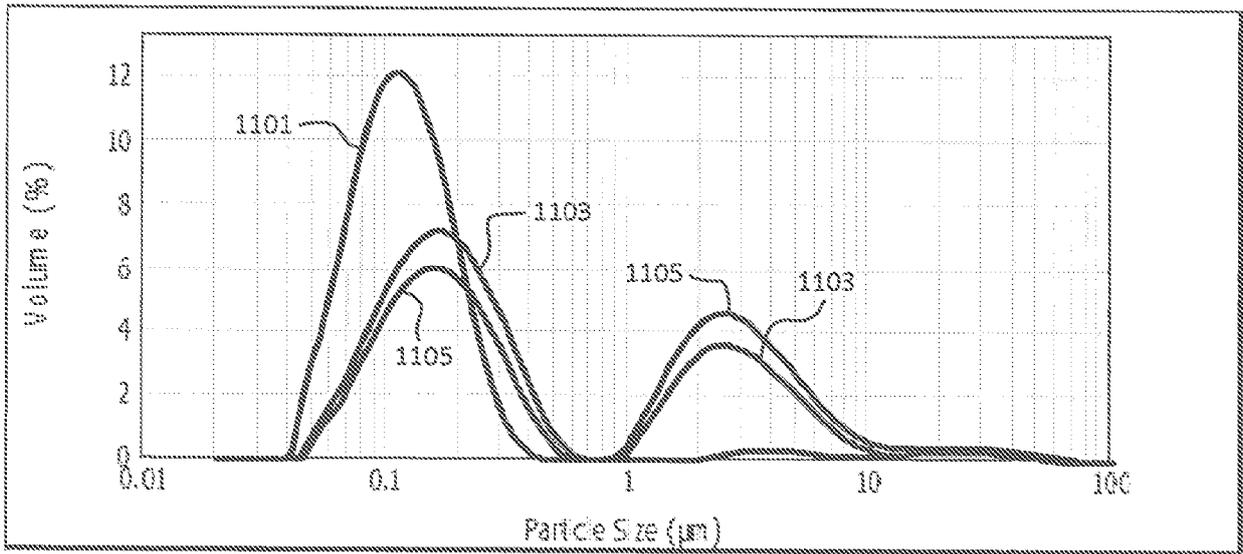


Fig. 11

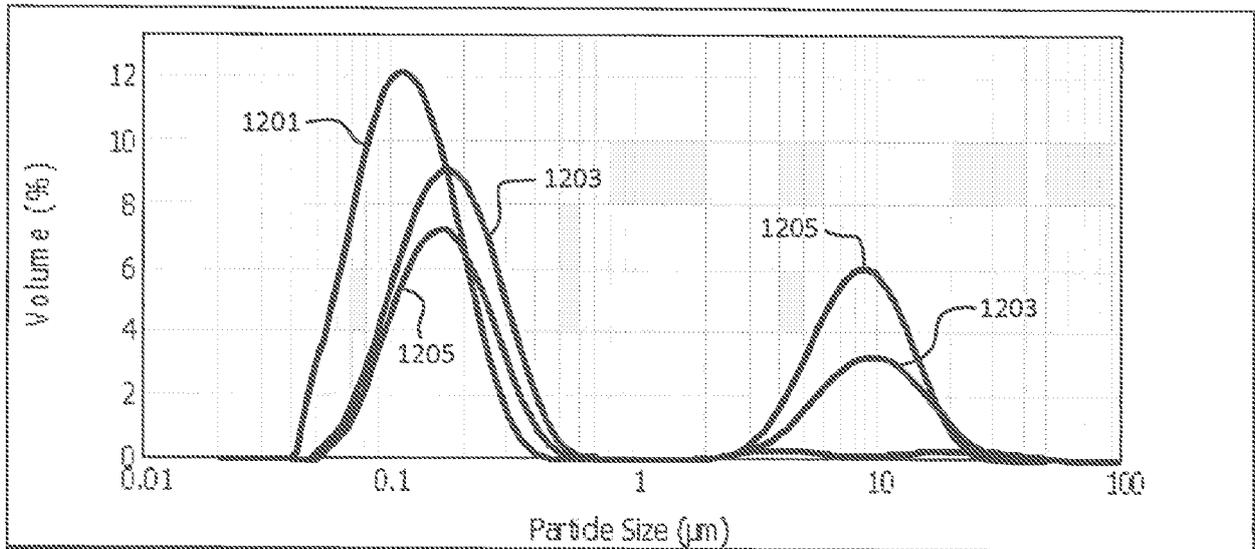


Fig. 12

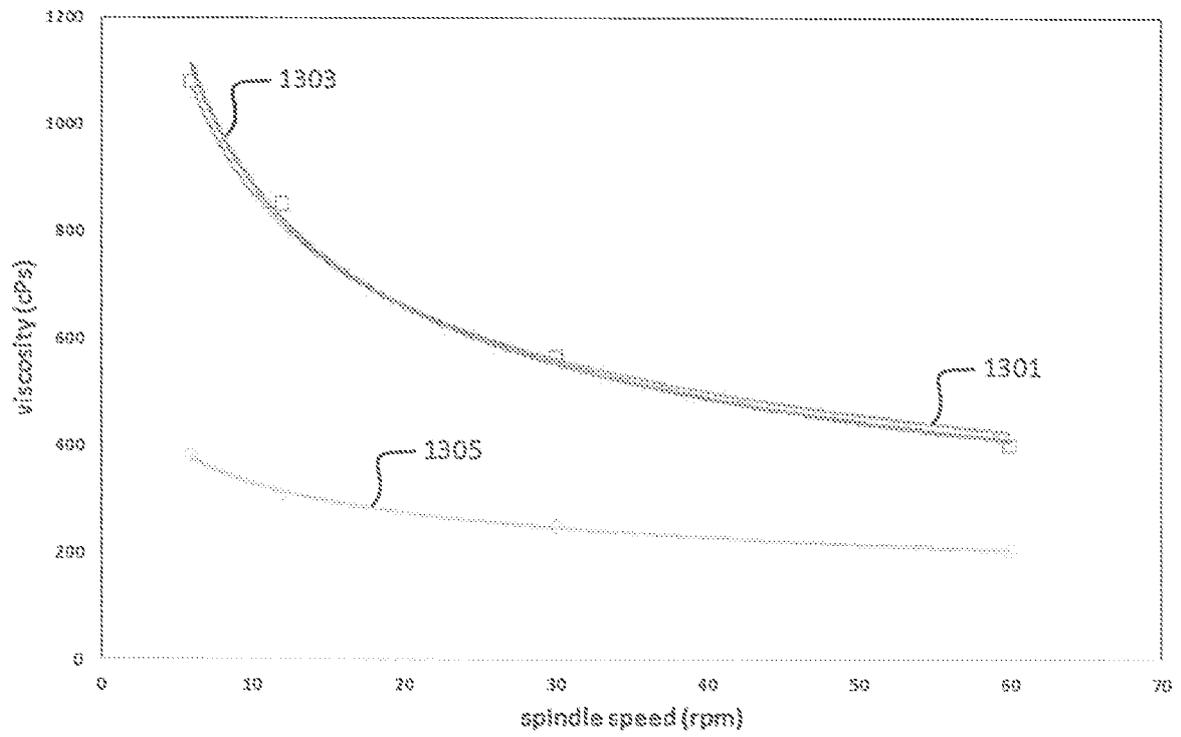


Fig. 13

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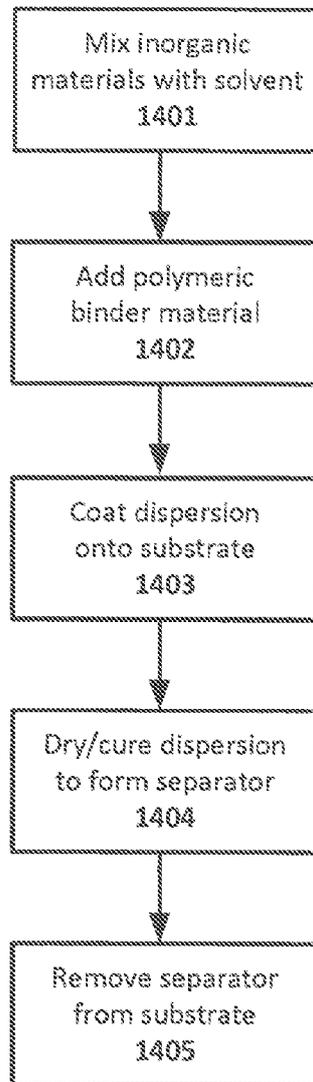


Fig. 14

## INTERNATIONAL SEARCH REPORT

International application No.  
**PCT/US2014/035947****A. CLASSIFICATION OF SUBJECT MATTER****H01M 2/16(2006.01)i, H01M 10/05(2010.01)i, C08J 5/22(2006.01)i, C08K 3/00(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 2/16; B05D 5/12; H01M 4/36; H01M 2/18; H01M 4/04; H01M 10/05; C08J 5/22; C08K 3/00Documentation 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 modelsElectronic data base consulted during the international search (name of data base and, where practicable, search terms used)  
eKOMPASS(KIPO internal) & Keywords: separator, porous, ceramic particle, pore-size, PVdF, polymer and shrinkage**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2007-0009803 A1 (JIN-HEE KIM et al.) 11 January 2007 See abstract, paragraphs [0024], [0047]-[0048], [0059], [0071], [0109] and claims 1, 7, 18-19.	1-3, 7-26
A		27-28
Y	US 2013-0089770 A1 (SATOSHI NISHIKAWA) 11 April 2013 See abstract, paragraphs [0034]-[0035] and claim 1.	1-3, 7-26
A	KR 10-2011-0116489 A (KOREA INSTITUTE OF SCIENCE AND TECHNOLOGY) 26 October 2011 See abstract, paragraphs [0016], [0026]-[0034] and claim 1.	1-3, 7-28
A	KR 10-2012-0062333 A (HYUNDAI MOTOR COMPANY) 14 June 2012 See abstract, paragraphs [0051]-[0056] and claims 1, 8, 11.	1-3, 7-28
A	US 2009-0269489 A1 (VOLKER HENNIGE et al.) 29 October 2009 See abstract, paragraphs [0078]-[0079] and claim 19.	1-3, 7-28

 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

"&amp;" document member of the same patent family

Date of the actual completion of the international search

05 September 2014 (05.09.2014)

Date of mailing of the international search report

**05 September 2014 (05.09.2014)**

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/US2014/035947****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.: 4-6  
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 additional 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/US2014/035947**

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