(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
21 September 2017 (21.09.2017)

WIPO | PCT

(10) International Publication Number
WO 2017/160897 A1

(51) International Patent Classification:
*H01M 10/0525* (2010.01) *B32B 15/04* (2006.01)
*B24B 1/00* (2006.01) *H01G 11/04* (2013.01)
*B32B 9/04* (2006.01) *H01G 11/22* (2013.01)

(21) International Application Number:
PCT/US2017/022388

(22) International Filing Date:
15 March 2017 (15.03.2017)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
62/310,030 18 March 2016 (18.03.2016) US

(71) Applicant: **3M INNOVATIVE PROPERTIES COMPANY** [US/US]; 3M Center, Post Office Box 33427, Saint Paul, Minnesota 55133-3427 (US).

(72) Inventors: **CHEVIER, Vincent J.**; 3M Center, Post Office Box 33427, Saint Paul, Minnesota 55133-3427 (US). **BARTLING, Brandon A.**; 3M Center, Post Office Box 33427, Saint Paul, Minnesota 55133-3427 (US). **HAJIME, Evan K.**; 3M Center, Post Office Box 33427, Saint Paul, Minnesota 55133-3427 (US). **DIVIGALPITIYA, Ranjith**; 1840 Oxford Street East, London, Ontario N5V 3R6 (CA).

(74) Agents: **BRAMWELL, Adam M.** et al.; 3M Center, Office of Intellectual Property Counsel, Post Office Box 33427, Saint Paul, Minnesota 55133-3427 (US).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KH, KN, KP, KR, 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.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK,

*[Continued on next page]*

(54) Title: SEPARATORS FOR HIGH DENSITY ELECTROCHEMICAL ENERGY STORAGE

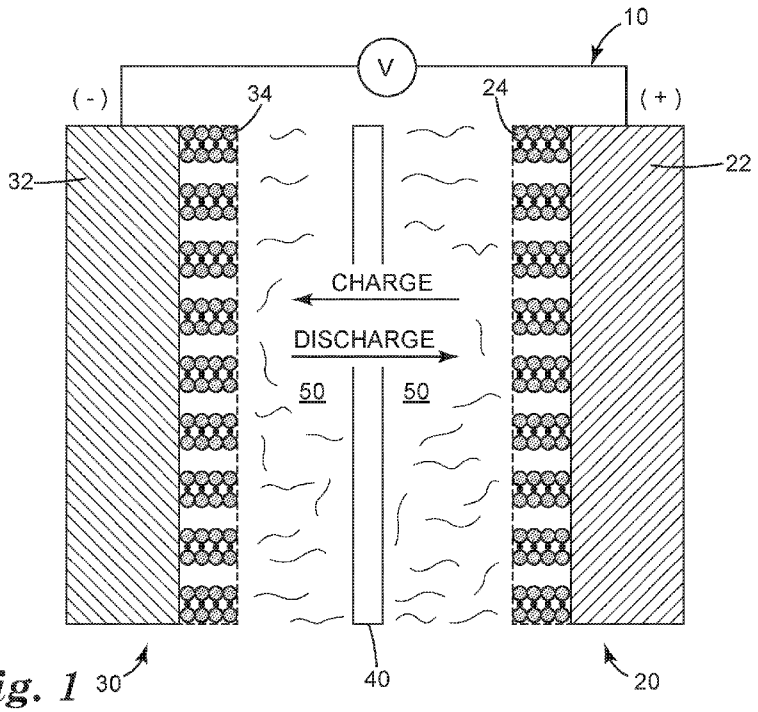



*Fig. 1*

(57) Abstract: A separator for an electrochemical cell includes a base layer configured to block electronic flow and allow ionic flow between a positive electrode and a negative electrode. The base layer has a first major surface and a second major surface. The separator further includes a layer of an exfoliatable material disposed on either or both of the first and second major surfaces. The layer of the exfoliatable material is provided on the base layer at an average thickness of between 1 and 500 nanometers. The layer of the exfoliatable material is binder-free.

WO 2017/160897 A1

SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

**Declarations under Rule 4.17**:

— *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*

— *as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))*

**Published**:

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

# SEPARATORS FOR HIGH DENSITY ELECTROCHEMICAL ENERGY STORAGE

## FIELD

The present disclosure relates to articles useful as separators in high energy density storage devices (e.g., rechargeable lithium ion batteries).

## BACKGROUND

Various separators have been introduced for use in electrochemical energy storage devices (e.g. lithium-ion batteries). Such separators are described, for example, in U.S. Pat. 6,432,586, PCT Pub. WO 2013/044545, U.S. Pub. 2014/0045033 and U.S. Pub. 2015/0079450.

## SUMMARY

In some embodiments, a separator for an electrochemical cell is provided. The separator includes a base layer configured to block electronic flow and allow ionic flow between a positive electrode and a negative electrode. The base layer has a first major surface and a second major surface. The separator further includes a layer of an exfoliatable material disposed on either or both of the first and second major surfaces. The layer of the exfoliatable material is provided on the base layer at an average thickness of between 1 and 500 nanometers. The layer of the exfoliatable material is binder-free.

In some embodiments, an electrochemical cell is provided. The electrochemical cell includes a positive electrode, a negative electrode, and the above described separator. The electrochemical cell further includes an electrolyte in ionic communication with the positive electrode and the negative electrode via the separator.

In some embodiments, a method of making an electrochemical cell is provided. The method includes providing a positive electrode that includes a positive electrode that includes lithium. The method further includes providing a negative electrode, providing an electrolyte comprising lithium, and providing the above described separator. Still further, the method includes incorporating the positive electrode, negative electrode, electrolyte, and the separator into an electrochemical cell. The electrolyte is in ionic communication with the positive electrode and the negative electrode via the separator.

In some embodiments, an electrochemical cell is provided. The electrochemical cell includes a positive electrode, a negative electrode, and a separator. The separator includes a base layer configured to block electronic flow and allow ionic flow between the positive electrode and the negative electrode. The electrochemical cell further includes a layer of an exfoliatable material interposed between either or both of (i) the separator and the positive electrode, or (ii) the separator and the negative electrode. The layer of the exfoliatable material is provided at an average thickness of between 1 and 500 nanometers. The layer of the exfoliatable material is binder-free. Still further, the electrochemical cell includes an electrolyte in ionic communication with the positive electrode and the negative electrode via the separator.

The above summary of the present disclosure is not intended to describe each embodiment of the present disclosure. The details of one or more embodiments of the disclosure are also set forth in the description below. Other features, objects, and advantages of the disclosure will be apparent from the description and from the claims.

## BRIEF DESCRIPTION OF THE DRAWINGS

The disclosure may be more completely understood in consideration of the following detailed description of various embodiments of the disclosure in connection with the accompanying figures, in which:

Figure 1 is a schematic of an electrochemical cell in accordance with some embodiments of the present disclosure.

Figure 2 is a schematic of a cross-section view of a separator in accordance with some embodiments of the present disclosure.

Figure 3 is a scanning electron microscope (SEM) image of an embodiment of the present disclosure.

Figure 4 shows the discharge capacity per gram of cathode material as a function of cycling of embodiments of the present disclosure.

Figure 5 shows plating of lithium in a coin cell for an embodiment of the present disclosure and a comparative example.

Figure 6 shows charge capacity versus cycle number for an embodiment of the present disclosure and a comparative example.

Figures 7A-7B show schematic plan views of patterned separators in accordance with some embodiments of the present disclosure.

Figure 8 is a plot of voltage vs. capacity for coin cells having separators in accordance with some embodiments of the present disclosure.

Figure 9 is a plot of voltage vs. capacity for coin cells having separators in accordance with some embodiments of the present disclosure.

Figures 10A-10D are photographs of the separators of Examples 17-18 and Comparative Examples 5-6, after high temperature storage.

Figure 11 is a FESEM image of the cross section of the first major surface of the separator of Example 6.

Figure 12 is a FESEM image of the cross section of the second major surface of the separator of Example 6.

## DETAILED DESCRIPTION

Traditional separators for lithium-ion batteries include polyolefin (e.g. polyethylene, polypropylene) films having thicknesses between 10 and 30 μm. More recently, ceramic coated separators have been introduced in the lithium-ion battery industry to address a number of issues. For example, ceramic coatings are intended to improve safety and performance by making the separator more electrochemically and mechanically stable. Generally, the ceramic coating of such separators include a binder material and an inorganic material dispersed in the binder. The ceramic coatings are generally thicker than 2 μm, with a typical thickness of 3 μm.

While an improvement over traditional separators, ceramic coated separators are associated with several drawbacks. For example, the increased thickness of the separator (as a result of the ceramic coating) results in batteries having lower energy densities. Also, it has been observed that the ceramic coatings can reduce the porosity of the separator which, in turn, may negatively impact the rate capability of the cell. Still further, it has been observed that the binder of the ceramic coated separators can be subject to electrochemical instability. Consequently, separators useful in high energy rechargeable batteries, which improve upon the foregoing drawbacks may be desirable.

As used in the present disclosure,

the terms "charge" and "charging" refer to a process for providing electrochemical energy to a cell;

the terms "discharge" and "discharging" refer to a process for removing electrochemical energy from a cell, e.g., when using the cell to perform desired work;

the phrase "charge/discharge cycle" refers to a cycle wherein an electrochemical cell is fully charged, i.e. the cell attains it's upper cutoff voltage and the cathode is at about 100% state of charge, and is subsequently discharged to attain a lower cutoff voltage and the cathode is at about 100% depth of discharge;

the phrase "positive electrode" refers to an electrode (often called a cathode) where electrochemical reduction and lithiation occurs during a discharging process in a full cell

the phrase "negative electrode" refers to an electrode (often called an anode) where electrochemical oxidation and delithiation occurs during a discharging process in a full cell;

the term "alloy" refers to a substance that includes any or all of metals, metalloids, or semimetals; and

the phrase "electrochemically active material" refers to a material, which can include a single phase or a plurality of phases, that can electrochemically react or alloy with lithium under conditions possibly encountered during charging and discharging in a lithium ion battery (e.g., voltages between 0 V and 2 V versus lithium metal).

As used herein, the singular forms "a", "an", and "the" include plural referents unless the content clearly dictates otherwise. As used in this specification and the appended embodiments, the term "or" is generally employed in its sense including "and/or" unless the content clearly dictates otherwise.

As used herein, the recitation of numerical ranges by endpoints includes all numbers subsumed within that range (e.g. 1 to 5 includes 1, 1.5, 2, 2.75, 3, 3.8, 4, and 5).

Unless otherwise indicated, all numbers expressing quantities or ingredients, measurement of properties and so forth used in the specification and embodiments are to be understood as being modified in all instances by the term "about." Accordingly, unless indicated to the contrary, the numerical parameters set forth in the foregoing specification and attached listing of embodiments can vary depending upon the desired properties sought to be obtained by those skilled in the art utilizing the teachings of the present disclosure. At the very least, and not as an attempt to limit the application of the doctrine

of equivalents to the scope of the claimed embodiments, each numerical parameter should at least be construed in light of the number of reported significant digits and by applying ordinary rounding techniques.

In some embodiments, the present disclosure relates to articles useful as separators in high energy density rechargeable electrochemical energy storage devices (e.g., rechargeable lithium ion batteries). Electrochemical energy storage devices can include, for example, Li-ion cells, Li-metal cells, Li-sulfur cells, Li-air cells, Na-ion cells, Mg-ion cells, Zn-air cells, NiMH cells, Lead-acid cells, or electrochemical capacitors or supercapacitors. FIG. 1 shows an exemplary schematic cross sectional view of an Li-ion electrochemical cell, in which 10 represents the external connections to the cell, 20 represents the positive electrode with an active material 24 coated onto a positive current collector 22, 30 represents the negative electrode with an active material 34 coated onto negative current collector 32, 40 represents a separator, and 50 represents an electrolyte. Generally, during charging and discharging of the electrochemical cell, ions move through a charge carrying medium of the electrolyte 50, via the separator 40, between the positive electrode 20 and the negative electrode 30 (i.e., the electrolyte is in ionic communication with the positive electrode and the negative electrode via the separator). For example, when the electrochemical cell is discharged, lithium ions flow from the negative electrode 30 to the positive electrode 20. In contrast, when the electrochemical cell is charged, lithium ions flow from the positive electrode 20 to the negative electrode 30.

In some embodiments, as shown in FIG. 2, a separator 40 may include a base layer 45 having a first major surface 45a, and a second major surface 45b opposite the first major surface 45a. Either or both of the first major surface 45a and the second major surface 45b may bear thereon an exfoliatable material 47.

In some embodiments, the base layer 45 may be configured to block electronic flow yet permit ionic flow between the positive electrode and negative electrode. For example, the base layer 45 may be formed of or include an electrically insulating polymer that has sufficient porosity for ions to flow into and through the base layer 45. In some embodiments, the base layer 45 may consist essentially of one layer of material, or it may have a multilayered construction. For example, the base layer 45 may include a plurality of layers, or layer stack, with the individual layers of the stack being coupled to one another with a suitable fastening mechanism (e.g, adhesive). The base layer (or any

individual layer of the layer stack) may have any shape and thickness. The thickness of the base layer 45 (i.e., the dimension of the base layer in a direction normal to the first and second major surfaces) may be between 5 and 50 μm, between 8 and 30 μm, between 8 and 25 μm, or between 8 and 16 μm.

In illustrative embodiments, the base layer 45 may be formed of polymeric materials. In some embodiments, the base layer 45 may be formed of porous or microporous polymeric materials. In some embodiments, the base layer may be formed of electrically insulating polymers. Suitable polymeric materials for the base layer 45 may include polyolefins, polyvinylidene fluoride (PVDF), polytetrafluoroethylene (PTFE), polyamides, or cellulosic polymers. Suitable polyolefins include polypropylene, polyethylene. In some embodiments, the base layer 45 may include a three layer construction that include a polypropylene layer disposed between two polypropylene layers. In some embodiments, the base layer 45 may have a porosity of between 20-80%, between 28-60%, or between 30-50%. The base layer 45 may have an average pore size of between 0.02 to 5 microns, between 0.02 to 2 microns, or between 0.08 to 0.5 microns.

In some embodiments, the exfoliatable material 47 may be disposed on any portion, up to the entirety of, either or both of the first major surface 45a and the second major surface 45b. For example, the exfoliatable material 47 may be disposed on at least 50%, 75%, 90%, 95%, or 99% of either or both of the first major surface 45a and the second major surface 45b, based on the total area of the respective surface. In some embodiments, the exfoliatable material 47 may be disposed on any portion, up to the entirety of, only one of the first major surface 45a and the second major surface 45b.

For purposes of the present application, the term "exfoliatable material" means a material that breaks up into flakes, scales, sheets or layers upon application of shear force (or was formed from a form of the material (e.g., particles) that broke up into flakes, scales, sheets, or layers upon application of shear force). In some embodiments, the exfoliatable material 47 may be an inorganic exfoliatable material. The exfoliatable material 47 may include a material that is electrically insulating or electrically conductive. The exfoliatable material 47 may be a blend of materials, individually electrically insulating and/or electrically conductive. In some embodiments an electrically conductive exfoliatable material may be disposed on the first major surface 45a and an electronically insulating exfoliatable material may be disposed on the second major surface 45b.

In various embodiments, the exfoliatable material 47 may have a layered, planar atomic structure, in which atoms in the layers are bonded covalently and or ionically. Bonding between layers may be via weak van der Waals bonds, which allows layers to be easily separated, or to slide past each other.

In some embodiments, the exfoliatable material 47 may include hexagonal boron nitride (e.g., hexagonal boron nitride flakes), graphite (e.g., graphite flakes), molybdenum disulfide, or clay.

In various embodiments, the exfoliatable material 47 may be present as a layer or layering of particulates. As used herein, the term "particulate" means discrete, non-fibrous particles. The average longest dimension of the particulates may be between 0.1 and 100 μm, 1 and 20 μm, or 5 and 15 μm. The average shortest dimension of the particulates may be between 0.001 and 1 μm, or between 0.01 and 0.1 μm. In some embodiments, the exfoliatable material 47 may have a Mohs' hardness (as reported in CRC Handbook of Chemistry and Physics 78th Edition (1998) , CRC Press NY p 12-205) of between 0.4 and 8, or between 0.4 and 3.

In some embodiments, the exfoliatable material 47 may be binder-free. For purposes of the present disclosure, a material can act as a binder if it acts as a mechanism for attaching the exfoliatable material 47 to a substrate (e.g., the base layer 45). The term "binder-free" means there is no binder material or a binder material is present in only trace amounts, i.e. a total of not more than one weight percent based on the total weight of the exfoliatable material. The absence of a binder material may allow for coatings having substantially reduced thickness. In this regard, in some embodiments, the exfoliatable material may be present in a layer having an average thickness (dimension of the layer in a direction normal to a major surface of the base layer) of between 1 and 500 nanometers, between 1 and 250 nanometers, between 10 and 200 nanometers, or between 10 and 100 nanometers.

In some embodiments, the separator may further include a composite ceramic layer. The composite ceramic layer may include a binder material and ceramic particles dispersed in the binder material. The ceramic particles may be inorganic or organic. Examples of suitable inorganic particles may include oxides of silicon, aluminum, zirconium, titanium, or zinc or mixtures thereof or carbonates of silicon, alumina, zirconium, calcium, zinc, and blends or mixtures thereof. In some embodiments, the

ceramic particles may include alumina. The inorganic particles may have an average particle size ranging from 0.05 to 5 μm, from 0.01 to 4 μm, or 0.01 to 2 μm in diameter (or length of longest dimsension). In some embodiments, the exfoliatable material 47 may be disposed on one of the first major surface 45a and the second major surface 45b, and the composite ceramic layer may be disposed on the other of the first major surface 45a and the second major surface 45b.

In some embodiments, the present disclosure is further directed to electrochemical cells that include the above-described battery separators. In addition to the above-described separators, the electrochemical cells may include a positive electrode, a negative electrode, and an electrolyte

In some embodiments, the positive electrode may include a current collector made of a conductive material such as a metal. According to an exemplary embodiment, the current collector includes aluminum or an aluminum alloy. According to an exemplary embodiment, the thickness of the current collector is 5 μm to 75 μm.

The positive electrode may include a layer of active material coated on the current collector. The layer of active material can be provided on only one side of the current collector or it may be provided or coated on both sides of the current collector. Suitable active materials for the positive electrode include lithium transition metal oxide intercalation compounds such as $LiCoO_2$, $LiCO_{0.2}Ni_{0.8}O_2$, $LiMn_2O_4$, $LiFePO_4$, $LiNiO_2$, or lithium mixed metal oxides of manganese, nickel, and cobalt in any proportion. Blends of these materials can also be used in positive electrode compositions. Other exemplary cathode materials are disclosed in U.S. Patent No. 6,680,145 (Obrovac et al.) and include transition metal grains in combination with lithium-containing grains. Suitable transition metal grains include, for example, iron, cobalt, chromium, nickel, vanadium, manganese, copper, zinc, zirconium, molybdenum, niobium, or combinations thereof with a grain size no greater than about 50 nanometers. The thickness of the active material of the positive electrode is typically 0.1 μm to 3 mm. According to other exemplary embodiments, the thickness of the active material is 10 μm to 300 μm. According to another exemplary embodiment, the thickness of the active material is 20 μm to 90 μm.

In some embodiments, the negative electrode may include a current collector made of a conductive material such as a metal. According to an exemplary embodiment, the current collector includes copper or a copper alloy. According to another exemplary

embodiment, the current collector is titanium or a titanium alloy. According to another exemplary embodiment, the current collector is nickel or a nickel alloy. According to another exemplary embodiment, the current collector is aluminum or an aluminum alloy. According to an exemplary embodiment, the thickness of the current collector is 5 μm to 75 μm.

The negative electrode includes a layer of active material coated on the current collector. The layer of active material can be provided on only one side of the current collector or it may be provided or coated on both sides of the current collector. Typically, the active material of the negative electrode includes a carbonaceous material (e.g., carbon such as graphite), a silicon or silicon alloy material, a lithium material, a titanate material, or a combination thereof. The thickness of the active material of the negative electrode is typically 0.1 μm to 3 mm. According to other exemplary embodiments, the thickness of the active material is 10 μm to 300 μm. According to another exemplary embodiment, the thickness of the active material is 20 μm to 90 μm.

While the present disclosure has been described with respect to embodiments in which the exfoliatable layer 47 is provided on a major surface of the base layer 45, it is to be appreciated that the exfoliatable layer 47 may be disposed in the electrochemical cell in any position within the electrochemical cell such that the exfoliatable layer 47 is interposed between the base layer 45 and the positive electrode and/or interposed between the base layer 45 and the negative electrode.

In various embodiments, useful electrolyte compositions may be in the form of a liquid, solid, or gel. In embodiments in which the electrolyte compositions are in the form of a sold or gel, it is to be appreciated that the solid or gel electrolyte may also function as the base layer 45 of the separator. The electrolyte compositions may include a salt and a solvent (or charge-carrying medium). Examples of solid electrolyte solvents include polymers such as polyethylene oxide, polytetrafluoroethylene, fluorine-containing copolymers, and combinations thereof. Examples of liquid electrolyte solvents include ethylene carbonate (EC), diethyl carbonate (DEC), dimethyl carbonate (DMC), ethyl methyl carbonate (EMC), propylene carbonate, fluoroethylene carbonate (FEC), tetrahydrofuran (THF), acetonitrile, and combinations thereof. In some embodiments the electrolyte solvent may comprise glymes, including monoglyme, diglyme and higher glymes, such as tetraglyme Examples of suitable lithium electrolyte salts include $LiPF_6$,

$LiBF_4$, $LiClO_4$, lithium bis(oxalato)borate, $LiN(CF_3SO_2)_2$, $LiN(C_2F_5SO_2)_2$, $LiAsF_6$, $LiC(CF_3SO_2)_3$, and combinations thereof.

The disclosed lithium ion electrochemical cells can be used in a variety of devices including, without limitation, portable computers, tablet displays, personal digital assistants, mobile telephones, motorized devices (e.g., personal or household appliances and vehicles), instruments, illumination devices (e.g., flashlights) and heating devices. One or more lithium ion electrochemical cells of this disclosure can be combined to provide a battery pack.

The present disclosure further relates to methods of making the above described separators. The method may include providing a base layer, as described above. The method may then include coating the substrate with an amount of the exfoliatable material, as described above. In some embodiments, the step of coating the substrate may include depositing a dry, solvent-less or near solvent-less composition that includes particles of the exfoliatable material onto to the base layer. Thus, the composition to be applied may be provided in a solid particulate form, rather than in a liquid or paste form. The step of coating may then include buffing the dry, solvent-less composition on said base layer. As used herein, "buffing" refers to any operation in which a pressure normal to a subject surface (e.g., a major surface of a substrate) (e.g., a pressure greater than 0 and less than about 30 $g/cm^2$) coupled with movement (e.g., rotational, lateral, combinations thereof) in a plane parallel to said subject surface is applied.

In some embodiments, buffing may be carried out using any buffing apparatus known in the art (e.g., power sander, power buffer, orbital sander, random orbital sander) suitable for applying dry particles to a surface, or manually (i.e., by hand). An exemplary buffing apparatus may include a motorized buffing applicator (e.g., disc, wheel) which may be configured to apply a pressure normal to a subject surface as well as rotate in a plane parallel to said subject surface. The buffing applicator may include a buffing surface that contacts with, or is intended to contact with, the subject surface during a buffing operation. In some embodiments, the buffing surface may include metal, polymer, glass, foam (e.g., closed-cell foam), cloth, paper, rubber, or combinations thereof. In various embodiments, the buffing surface may include an applicator pad that may be made of any appropriate material for applying particles to a surface. The applicator pad may, for example, be made of woven or non-woven fabric or cellulosic material. The applicator

pad may alternatively be made of a closed cell or open cell foam material. In other cases, the applicator pad may be made of brushes or an array of nylon or polyurethane bristles. Whether the applicator pad comprises bristles, fabric, foam, and/or other structures, it may have a topography wherein particles of the exfoliatable material to be applied as a coating can become lodged in and carried by the applicator pad.

In some embodiments, the buffing apparatus may be configured to move in a pattern parallel to the subject surface and to rotate about a rotational axis perpendicular to the subject surface. The pattern may include a simple orbital motion or random orbital motion. Rotation of the buffing apparatus may be carried out as high as 100 orbits per minute, as high as 1,000 orbits per minute, or even as high as 10,000 orbits per minute. The buffing apparatus may be applied in a direction normal to the subject surface at a pressure of a least 0.1 $g/cm^2$, at least 1 $g/cm^2$, at least 10 $g/cm^2$, at least 20 $g/cm^2$, or even at least 30 $g/cm^2$.

The coating of exfoliatable material can be formed on or over a surface of the base layer in a number of ways. In one approach, the composition used to form the coating can first be applied directly to the surface, and then the buffing apparatus may contact the composition and the surface. In another approach, the composition can first be applied to the buffing surface of the buffing apparatus, and the particle-loaded buffing surface may then contact the surface of the base layer. In still another approach, a portion of the composition can be applied directly to the surface, and another portion of the composition can be applied to the buffing surface of the buffing apparatus, after which the particle-loaded buffing surface may contact the surface and remainder of the composition.

In some embodiments, the buffing operation of the present disclosure can be used to produce a high quality, thin layer or coating on or over a surface of the base layer. The thickness of the buffed coating may be controlled by controlling the buffing time. Generally, the thickness of the coating may increase linearly with buffing time after a certain rapid initial increase. The coating thickness may also be controlled by controlling the amount of the composition used during the buffing operation. In some embodiments, coating of the exfoliatable material can also be applied using methods as described in U.S. Patent 9,172,085, which is herein incorporated by reference in its entirety.

The present disclosure further relates to methods of making lithium ion electrochemical cells. In various embodiments, the method may include providing a

negative electrode as described above, providing a positive electrode as described above, and incorporating the negative electrode and the positive electrode into an electrochemical cell comprising a lithium-containing electrolyte and any of the above-described separators.

In accordance with the articles and methods of the present disclosure, separators for electrochemical cells which provide for improved cell performance are obtained. For example, in some embodiments, the separators of the present disclosure may extend the working life of lithium ion batteries by increasing the capacity retention. In some embodiments, the separators of the present disclosure may extend the working life of lithium ion batteries by improving shorting protection from lithium metal dendrite formation. In some embodiments, the separators of the present disclosure may increase energy density in lithium ion batteries by reducing the thickness of the separator compared to conventional coated separators. In some embodiments, the separators of the present disclosure may reduce the potential electrochemical instabilities associated with the presence of a binder in ceramic coated separators. In some embodiments, the separators of the present disclosure may reduce the oxidation of the base layer. In some embodiments the separators of the present disclosure may improve the wetting of the separator by the electrolyte.

Listing of Embodiments

1. A separator for an electrochemical cell, the separator comprising:

a base layer configured to block electronic flow and allow ionic flow between a positive electrode and a negative electrode, the base layer having a first major surface and a second major surface;

a layer of an exfoliatable material disposed on either or both of the first and second major surfaces;

wherein the layer of the exfoliatable material is provided on the base layer at an average thickness of between 1 and 500 nanometers; and

wherein the layer of the exfoliatable material is binder-free.

2. The separator according to embodiment 1, wherein the exfoliatable material comprises graphite or hexagonal boron nitride.

3. The separator according to embodiment 1, wherein the exfoliatable material comprises an inorganic, electrically insulating material.

4. The separator according to embodiment 1, wherein the exfoliatable material comprises an electrically conductive material.

5. The separator according to any one of the previous embodiments, wherein the exfoliatable material has a Mohs' hardness of between 0.4 and 3.

6. The separator according to any one of the previous embodiments, wherein the layer of the exfoliatable material is provided on the base layer at an average thickness of between 1 and 100 nanometers.

7. The separator according to any one of the previous embodiments, wherein the base layer comprises a microporous polymeric material.

8. The separator according to any one of the previous embodiments, wherein the base layer comprises polyethylene.

9. The separator according to any one of the previous embodiments, wherein the base layer comprises polypropylene.

10. The separator according to any one of the previous embodiments, wherein the base layer has an average thickness of between 8 and 25 μm.

11. An electrochemical cell comprising:
a positive electrode;
a negative electrode;
a separator according to any one of embodiments 1 - 10; and
an electrolyte in ionic communication with the positive electrode and the negative electrode via the separator.

12. An electronic device comprising the electrochemical cell according to embodiment 11.

13. A method of making an electrochemical cell, the method comprising:

providing a positive electrode comprising a positive electrode composition comprising lithium;

providing a negative electrode;

providing an electrolyte comprising lithium;

providing a separator according to any one of embodiments 1 - 10; and

incorporating the positive electrode, negative electrode, the electrolyte, and the separator into an electrochemical cell;

wherein the electrolyte is in ionic communication with the positive electrode and the negative electrode via the separator.

14. An electrochemical cell comprising:

a positive electrode;

a negative electrode;

a separator comprising a base layer configured to block electronic flow and allow ionic flow between the positive electrode and the negative electrode;

a layer of an exfoliatable material interposed between either or both of (i) the separator and the positive electrode, or (ii) the separator and the negative electrode, wherein layer of the exfoliatable material is provided at an average thickness of between 1 and 500 nanometers, and wherein the layer of the exfoliatable material is binder-free; and

an electrolyte in ionic communication with the positive electrode and the negative electrode via the separator.

15. The electrochemical cell according to embodiment 14, wherein the exfoliatable material comprises graphite or hexagonal boron nitride.

16. The electrochemical cell according to embodiment 14, wherein the exfoliatable material comprises hexagonal boron nitride.

The operation of the present disclosure will be further described with regard to the following detailed examples. These examples are offered to further illustrate various specific embodiments and techniques. It should be understood, however, that many variations and modifications may be made while remaining within the scope of the present disclosure.

## EXAMPLES

The following examples are offered to aid in the understanding of the present disclosure and are not to be construed as limiting the scope thereof. Unless otherwise indicated, all parts and percentages are by weight.

### Test Methods and Preparation Procedures

The following test methods and protocols were employed in the evaluation of the comparative and illustrative examples that follow.

Coin full cell assembly

Coin full cells for Comparative Examples CE1 and CE2 and Examples 1-10 and 12 were assembled using a graphite anode and an NMC cathode. The cathode was 94% by weight (wt%) $Li(Ni_{0.6}Mn_{0.2}Co_{0.2})O_2$ (NMC622, available as HX12 from Umicore, Brussels, Belgium), 3.5 wt% polyvinylidene fluoride (PVdF, Kynar 461 from Arkema Inc. Colombe, France), 1.25 wt% conductive carbon (SUPER P from Imerys graphite and Carbon, Switzerland), 1.25 wt% flake graphite (KS6L from Imerys graphite and Carbon, Switzerland) coated on 20 μm aluminum (Toyo Aluminum K.K., Osaka, Japan) , with a first delithiation capacity of approximately 3.1 $mAh/cm^2$. The anode was 96 wt% graphite (MAG-E from Hitachi Chemical, Osaka Japan), 2.2 wt% Styrene-Butadiene Rubber (SBR, BM-480B from Zeon Corporation, Tokyo, Japan), 1.8 wt% Sodium Carboxymethyl Cellulose (CMC, Grade 2200 from Daicel FineChem Ltd.,Tokyo, Japan) coated on 15 μm copper (NC-WS, Furukawa Electric Co., Tokyo, Japan) with a first lithiation capacity of approximately 4.6 $mAh/cm^2$. The coin full cells had an N/P ratio of approximately 1.5.

Electrochemical 2325 type coin full cells for CE 1, CE2, and Examples 1-10 and 12 were prepared as follows. Disks (16 mm in diameter) were cut from the anode and cathode electrode coatings for use in 2325-button cells. Each 2325 cell contained a 18 mm

diameter disk of Cu as a spacer (900 μm thick), a 16 mm diameter disk of the anode electrode, and one or more 20 mm diameter microporous separators as described below, a 16 mm diameter disk of the cathode electrode, and a 18 mm aluminum spacer (900 μm thick). One hundred micro liters (μL) of electrolyte solution (90 wt% SELECTILYTE LP 57 available from BASF, Independence, OH, 10 wt% fluoroethylene carbonate (FEC) available from Fujian Chuangxin Science and Technology Development, LTP, Fujian, China) was used.

The coin cells were then cycled at 45°C using a Maccor 4000 Series charger (available from Maccor Inc, Tulsa, OK). The first cycle was performed at C/10 with a C/40 trickle at 5mV and a delithiation up to 1.5V, subsequent cycles were performed at C/4 with a C/20 trickle at 5 mV and a delithiation up to 0.9 V.

Li/Li cell assembly

Li/Li cells (2325 type) for Comparative Example CE3 and Example 11 were prepared as follows. Disks (14 mm diameter) were cut from Li foil (0.38 mm thick lithium ribbon; Aldrich Chemicals, Milwaukee, WI) for use in 2325-button cells. Each 2325 cell contained a 18 mm diameter disk of Cu as a spacer (900 μm thick), a 14 mm diameter disk of Li, one separator as detailed in the examples, 14 mm diameter disk of lithium (0.38 mm thick lithium ribbon from Aldrich Chemicals, Milwaukee, WI) and an 18 mm copper spacer (900 μm thick). 100 μL of electrolyte solution (90 wt% SELECTILYTE LP 57 available from BASF, Independence OH, 10 wt% FEC) was used.

To test the cells for the growth of dendrites, the coin cells were discharged at 22°C with a current of 1 mA until a shorting event occurred, indicating dendrite growth.

Cathode half cell assembly

Cathode half cells for Examples 18 and 19 and Comparative Examples CE5 and CE6 were prepared as follows. Disks (16 mm in diameter) were cut from the cathode electrode coatings for use in 2325-button cells. Each 2325 cell contained a 18 mm diameter disk of aluminum as a spacer (900 μm thick), a 16 mm diameter disk of the cathode, and one or more 20 mm diameter microporous separators as described below, a 18 mm diameter disk of Li (0.38 mm thick lithium ribbon; Aldrich Chemicals, Milwaukee, WI), and a 18 mm copper spacer (900 μm thick). One hundred micro liters (μL) of

electrolyte solution (90 wt% SELECTILYTE LP 57 available from BASF, Independence, OH, 10 wt% fluoroethylene carbonate (FEC) available from Fujian Chuangxin Science and Technology Development, LTP, Fujian, China) was used. The cathode was 94 wt% NMC622, 3.5 wt% PVDF, 1.25 wt% SUPER P, 1.25 wt% KS6L. The loading of the cathode was 16 mg/cm$^2$.

The cathode half cells were then cycled at 45°C using a Novonix ultra-high precision cycler (available from Novonix Battery Testing Services Inc., Dartmouth, NS, Canada). The cells were charged at 0.2 mA up to their upper cutoff voltage ( UCV) then discharged at 0.2 mA to 3.0V. Then charged at 0.2 mA to the UCV, then stored open circuit for 180 hours. The cells were tehn disassembled in a dry room with a dew point of less than -40°C. The separators were removed from the cells and rinsed in DMC and left to air dry.

Evaluation of Porosity of Separators

To test the impact of the coatings of the present disclosure on the porosity of separators, the separators were placed in a Gurley 4410N apparatus (Gurley Precision Instruments, Troy, NY). The time per volume of water displaced on setting 10 was recorded.

Evaluation of Wetting of Separators

To test the impact of the coatings of the present disclosure on the wetting of separators by an electrolyte, the separators were taped to a board held at an angle of 33 degrees with respect to horizontal and a 10 μL drop of SELECTILYTE LP57 was dropped onto the separator. The distance the drop travelled was used as an indication of the wetting of the separator: a relatively shorter distance of travel indicates better wetting of the separator. Drop travel was determined as the distance until the electrolyte drop disappeared into the separator.

**Preparation of Separators and Exemplary Electrochemical Cells**

Comparative Example 1 (CE1): A coin full cell was assembled as described above with one CELGARD 2325 (available from Celgard LLC, Charlotte, USA) separator,

which is a 25 μm thick trilayer Li-ion battery separator with a polypropylene (PP) / polyethylene (PE) / PP construction, synthesized using the so-called "dry-process".

Comparative Example 2 (CE2): A coin full cell was assembled as described above with one CELGARD C210 separator (available from CELGARD LLC, Charlotte, USA), which is a 16 μm thick PE monolayer Li-ion battery separator.

Coating Method

Coatings of hexagonal boron nitride or graphite powder on various substrates were prepared by gently polishing the powders onto substrates by hand using foam polishing pads (obtained from Meguiar's Inc., Irvine, CA under the trade designation "G3508 DA POLISHING POWER PADS"). Polishing was performed both orbitally and linearly, and each region of the substrate was contacted at least 8 times throughout the entire process. Compressed air (at 10 psi air pressure using a Silvent air gun, Model 007-L NPT, Silvent, Boras, Sweden) was used to remove loosely adherent excess particles after coating. Substrates were taped at the edges onto an aluminum sheet prior to polishing the desired side of the substrate, and the tape was carefully removed after cleaning the substrate with compressed air as described above.

Hexagonal boron nitride (hBN) powder with average particle size of 15 μm (obtained from 3M Technical Ceramics, Kempten, Germany under trade designation "3M BORON NITRIDE COOLING FILLERS") was used as received. Hexagonal boron nitride powder with average particle size of 1 μm (obtained from Aldrich Chemical Co., Inc., Milwaukee, WI) was used as received. Graphite (obtained from Asbury Carbons, Asbury, NJ, under the trade designation "MICROFYNE") was used as received.

Example 1: A piece of CELGARD 2325 was coated, using the Coating Method, with hexagonal boron nitride (hBN) on both sides using 15 μm hexagonal boron nitride (hBN) powder as a starting material. A thickness measurement with a Mitutoyo micrometer having a 1 μm accuracy was not able to detect an increase in thickness in comparison to the uncoated separator. Both the uncoated and coated separators were 25 ± 1 μm.

Example 2: A piece of CELGARD 2325 was coated, using the Coating Method, with hBN on one side using 15 μm hBN powder as a starting material. A thickness measurement with a Mitutoyo micrometer having a 1 μm accuracy was not able to

measure an increase in thickness. Both the uncoated and coated separators were 25 ± 1 μm.

Example 3: A piece of CELGARD C210 was coated, using the Coating Method, with hBN on both sides using 15 μm hBN powder as a starting material. A thickness measurement with a Mitutoyo micrometer having a 1 μm accuracy was not able to measure an increase in thickness. Both the uncoated and coated separators were 16 ± 1 μm.

Example 4: A piece of CELGARD C210 was coated, using the Coating Method, with hBN on one side using 15 μm hBN powder as a starting material. A thickness measurement with a Mitutoyo micrometer having a 1 μm accuracy was not able to measure an increase in thickness. Both the uncoated and coated separators were 16 ± 1 μm.

Example 5: A piece of CELGARD 2325 was coated, using the Coating Method, with hBN on both sides using 1 μm hBN powder as a starting material. A thickness measurement with a Mitutoyo micrometer having a 1 μm accuracy was not able to measure an increase in thickness. Both the uncoated and coated separators were 25 ± 1 μm.

Example 6: A piece of CELGARD C210 was coated, using the Coating Method, with hBN on both sides using 1 μm hBN powder as a starting material. A thickness measurement with a Mitutoyo micrometer having a 1 μm accuracy was not able to measure an increase in thickness. Both the uncoated and coated separators were 16 ± 1 μm.

Example 7: A piece of CELGARD 2325 was coated, using the Coating Method, with graphite on both sides using Microfyne graphite (Dixon Ticonderoga Company) as a starting material A thickness measurement with a Mitutoyo micrometer having a 1 μm accuracy was not able to measure an increase in thickness. Both the uncoated and coated separators were 25 ± 1 μm.

Example 8: A piece of CELGARD 2325 was coated, using the Coating Method, with graphite on one side using Microfyne graphite as a starting material. A thickness measurement with a Mitutoyo micrometer having a 1 μm accuracy was not able to measure an increase in thickness. Both the uncoated and coated separators were 25 ± 1 μm.

Example 9: A piece of CELGARD C210 was coated, using the Coating Method, with graphite on both sides using Microfyne graphite as a starting material. A thickness measurement with a Mitutoyo micrometer having a 1 μm accuracy was not able to measure an increase in thickness. Both the uncoated and coated separators were 16 ± 1 μm.

Example 10: A piece of CELGARD C210 was coated, using the Coating Method, with graphite on one side using Microfyne graphite as a starting material. A thickness measurement with a Mitutoyo micrometer having a 1 μm accuracy was not able to measure an increase in thickness. Both the uncoated and coated separators were 16 ± 1 μm.

Comparative Example 3 (CE3): Two Li/Li sister cells were assembled as described above with one C210 separator each.

Example 11: Two Li/Li sister cells were assembled and tested as described above with one Example 10 separator each.

Comparative Example 4 (CE4): A coin cell was assembled and cycled as in CE2, except that no anode was used. The "negative" side of the cell therefore consisted of only a PE separator facing a Cu spacer. Upon disassembly of the cells the Li was found to have plated on the Cu spacer.

Example 12: A coin cell was assembled and cycled as in CE4 except that the separator from Example 8 was used with the graphite side facing the Cu spacer. Upon disassembly of the cells the Li was found to have plated on the graphite-coated surface of the separator.

Example 13. Patterned coatings. A sample was prepared as in Example 10 except that the graphite was applied through a mask on the separator. The graphite coated region covered the area of the electrode but did not reach the edge of the cell. Li/Li cells were assembled as in Example 11.

Example 14. Mixed powders. A sample was prepared as in Example 10 except that at 50:50 weight ratio of hBN and graphite were applied to the surface of the separator. Li/Li cells were assembled as in Example 11.

Example 15. A Li/Li cell was assembled and tested as described above using one Example 3 separator.

Example 16. Two Li/Li cells were assembled and tested as described above using one Example 6 separator each.

Example 17: Asahi N316C separator (Asahi-Kasei Corporation, Tokyo, Japan), which is a 16 μm PE synthesized using the so-called wet-process, was coated, using the Coating Method, on both sides using 15 μm hBN powder as a starting material. The hBN coating can therefore be applied to separators obtained with the so-called wet-process.

Example 18: Cathode half cells were assembled as described in Methods using Example 15 as a separator and were cycled as described in Methods using a 4.2V UCV.

Example 19: Cathode half cells were assembled as described in Methods using Example 15 as a separator and were cycled as described in Methods using a 4.4V UCV.

Comparative Example 5: Cathode half cells were assembled as described in Methods using as-received Asahi 316C separator and were cycled as described in Methods using a 4.2V UCV.

Comparative Example 6: Cathode half cells were assembled as described in Methods using as-received Asahi 316C separator and were cycled as described in Methods using a 4.4V UCV.

**Results**

Figure 3 shows a scanning electron microscope (SEM) (TM-1000, Hitachi High-Technologies Corporation, Tokyo, Japan) image of Example 1. Thin hBN platelets are seen coating the CELGARD 2325. A voltmeter was used to confirm the insulating properties of Example 1 both in-plane and through-plane.

Figure 4 shows the discharge capacity per gram of cathode material as a function of cycling of Examples 3, 5, and 6, in comparison to CE1 and CE2. Figure 4 demonstrates that the coin full cells prepared using separators coated with hBN show higher capacity for at least 40 cycles versus the comparative examples.

Table 1 summarizes results from the electrolyte wetting test. Examples 1 and 3, which have been coated with 15 μm hBN powder, demonstrated a shorter distance of travel of the drop of electrolyte than CE1 and CE2, indicating better wetting of the separator by electrolyte.

**Table 1.** Electrolyte wetting test results.

| Example | Drop Travel (mm) |
|---|---|
| CE1 | 8.8 |
| CE2 | 7.5 |
| Ex. 1 | 5.3 |
| Ex. 3 | 4.6 |

Table 2 summarizes results from porosity testing. In order to maintain rate performance in a Li-ion battery the porosity of separators must remain high. Table 2 shows the porosities of the coated separators compared to the counter examples, showing that the ceramic coating only slightly decreases the porosity of the separator as opposed to traditional ceramic coatings which can significantly decrease porosity due to their thickness and use of binder.

**Table 2.** Time per volume as measured on a Gurley 4110N (Setting 10).

| Sample | CE1 | CE2 | Ex. 1 | Ex. 2 | Ex. 3 | Ex. 4 |
|---|---|---|---|---|---|---|
| 1 | 76.2 | 56.4 | 83.2 | 82.9 | 63.4 | 67.1 |
| 2 | 77.3 | 54.6 | 83.8 | 79.0 | 67.0 | 57.6 |
| 3 | 77.4 | 56.7 | 87.7 | 81.8 | 61.8 | 58.8 |
| Average | 77.0 | 55.9 | 84.9 | 81.2 | 64.1 | 61.2 |

The separators of Examples 7-10, which were coated with graphite, demonstrated no through-plane electronic conductivity but exhibited in-plane electric conductivity on the coated side(s), as determined by a hand held voltmeter.

Figure 5 compares voltage vs. capacity of duplicates of CE3 and Example 11 during discharge using a current of 1 mA. In both CE3 test cells, a shorting event occurred between 6 and 7 hours. Figure 5 shows this corresponds to a dendrite occurring after 3.8 to 4.5 $mAh/cm^2$ of Li plating. For Example 11, in both test cells a shorting event occurred after more than 15 hours. Figure 5 shows this corresponds to a dendrite occurring after more than 10 $mAh/cm^2$ of Li plating. The graphite coating of Example 11 therefore provided an improvement of greater than 2x in dendrite protection compared to CE3. Without being bound by theory, the presence of an electronically conducting layer on the surface of a separator may help reduce the presence of Li dendrites by providing a

constant potential across the interface and thereby reducing local variations in potential, which promote Li dendrite growth.

Figure 6 shows the charge capacity retention of Example 12 and CE4. These results demonstrate that the cell with the graphite coated separator (Example 12) has a much higher initial capacity than CE 4. Without being bound by theory, the graphite-coated surface may provide a favorable nucleation site which enables Li cells to function with no starting Li metal.

Figures 7A-7B show a patterned particulate coating in accordance with some embodiments of the present disclosure. As shown, the particulate coatings 50A and 50 B do not extend to the edge of the bare/uncoated base layers 55A and 55B. The pattern can be circular (Figure 7A) or linear in nature (Figure 7B) in order to be adapted to the shape of the electrode 60A, 60B.

Figure 8 shows that a patterned graphite, Example 13, coating yields a similar benefit as in Example 11 and dendrite shorting occurs after 8 $mAh/cm^2$, and that a mixed graphite/hBN coating, Example 14, yields an even better dendrite growth protection and dendrite shorting occurs after over 15 $mAh/cm^2$. Without being bound by theory, Example 14 achieves improved performance by combining the field leveling effect of graphite with the physical protection of hBN.

Figure 9 shows that double sided hBN, Examples 15 and 16, provide an even greater benefit than Examples 11, 12, 13, 14. Shorting occurs after nearly 30 $mAh/cm^2$ of Li has been plated compared to less than 5 mAh/cm2 for the Comparative Examples in Figure 5.

After cycling and storage at 45°C of Examples 17 and 18 and Comparative Examples 5 and 6, the cells were disassembled. The hBN coated separators of Examples 17 and 18 were noticeably easier to remove compared to the control separators in CE 5 and 6. The control separators (CE5 and CE6) stuck to the Li foil, symptomatic of considerable plating and Li dendrite penetrating the separator. The hBN separators also displayed significantly less black spotting, indicative of the polymer oxidation and subsequent carbonization. Figure 10 shows photographs of the separators after cell disassembly from Ex 17, 18 and CE 5, 6, visually indicating the benefit of the current invention in reducing Li dendrite penetration and separator oxidation.

Example 6 was cross-sectioned using an ion beam cross-section polisher (IB-19500CP, JEOL, Tokyo, Japan). Figure 11 shows a field emission scanning electron microscope (FESEM) (JSM-7600F, JEOL, Tokyo, Japan) image of the cross section of Example 6. A uniform coating of hBN is found on the PP base layer. The hBN coating is less than 0.5 μm thick (approximately 0.46 μm). Figure 12 shows an FESEM image of the same sample but the opposing face of the base layer, showing a uniform coating of hBN on the opposing PP base layer. The hBN coating is less than 0.2 μm thick (approximately 0.19 μm).

Although specific embodiments have been illustrated and described herein for purposes of description of some embodiments, it will be appreciated by those of ordinary skill in the art that a wide variety of alternate and/or equivalent implementations may be substituted for the specific embodiments shown and described without departing from the scope of the present disclosure.

What is Claimed:

1. A separator for an electrochemical cell, the separator comprising:

a base layer configured to block electronic flow and allow ionic flow between a positive electrode and a negative electrode, the base layer having a first major surface and a second major surface;

a layer of an exfoliatable material disposed on either or both of the first and second major surfaces;

wherein the layer of the exfoliatable material is provided on the base layer at an average thickness of between 1 and 500 nanometers; and

wherein the layer of the exfoliatable material is binder-free.

2. The separator according to claim 1, wherein the exfoliatable material comprises graphite or hexagonal boron nitride.

3. The separator according to claim 1, wherein the exfoliatable material comprises an inorganic, electrically insulating material.

4. The separator according to claim 1, wherein the exfoliatable material comprises an electrically conductive material.

5. The separator according to claim 1, wherein the exfoliatable material has a Mohs' hardness of between 0.4 and 3.

6. The separator according to claim 1, wherein the layer of the exfoliatable material is provided on the base layer at an average thickness of between 1 and 200 nanometers.

7. The separator according to claim 1, wherein the base layer comprises a microporous polymeric material.

8. The separator according to claim 1, wherein the base layer comprises polyethylene.

9. The separator according to claim 1, wherein the base layer comprises polypropylene.

10. The separator according to claim 7, wherein the base layer has an average thickness of between 8 and 25 μm.

11. An electrochemical cell comprising:

a positive electrode;

a negative electrode;

a separator according to claim 1; and

an electrolyte in ionic communication with the positive electrode and the negative electrode via the separator.

12. An electronic device comprising the electrochemical cell according to claim 11.

13. A method of making an electrochemical cell, the method comprising:

providing a positive electrode comprising a positive electrode composition comprising lithium;

providing a negative electrode;

providing an electrolyte comprising lithium;

providing a separator according to claim 1; and

incorporating the positive electrode, negative electrode, the electrolyte, and the separator into an electrochemical cell;

wherein the electrolyte is in ionic communication with the positive electrode and the negative electrode via the separator.

14. An electrochemical cell comprising:

a positive electrode;

a negative electrode;

a separator comprising a base layer configured to block electronic flow and allow ionic flow between the positive electrode and the negative electrode;

a layer of an exfoliatable material interposed between either or both of (i) the separator and the positive electrode, or (ii) the separator and the negative electrode, wherein the layer of the exfoliatable material is provided at an average thickness of between 1 and 500 nanometers, and wherein the layer of the exfoliatable material is binder-free; and

an electrolyte in ionic communication with the positive electrode and the negative electrode via the separator.

15. The electrochemical cell according to claim 14, wherein the exfoliatable material comprises graphite or hexagonal boron nitride.

16. The electrochemical cell according to claim 14, wherein the exfoliatable material comprises hexagonal boron nitride.

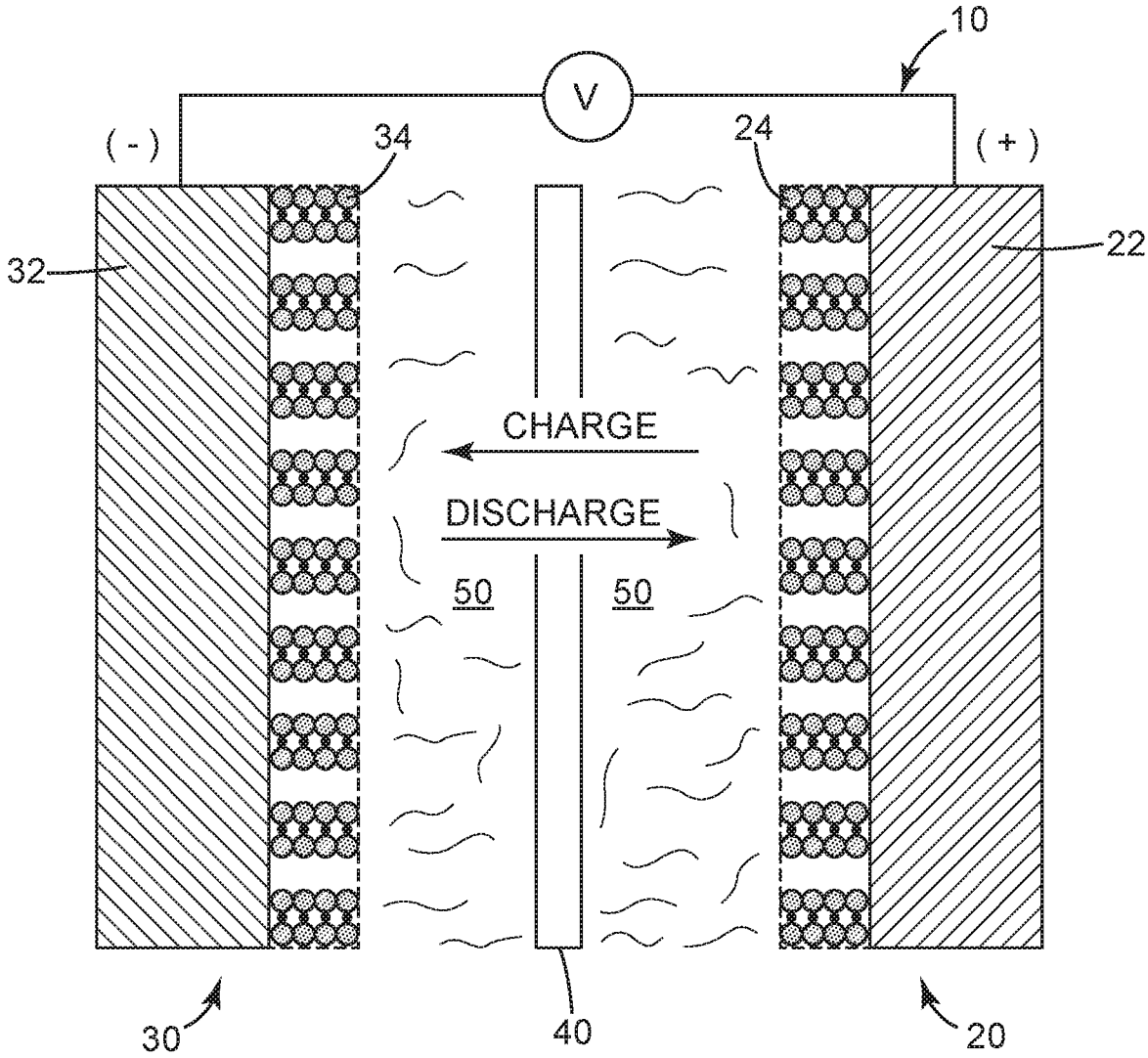

10
V
( - )
34
24
( + )
32
22
CHARGE
DISCHARGE
50
50
30
40
20

*Fig. 1*

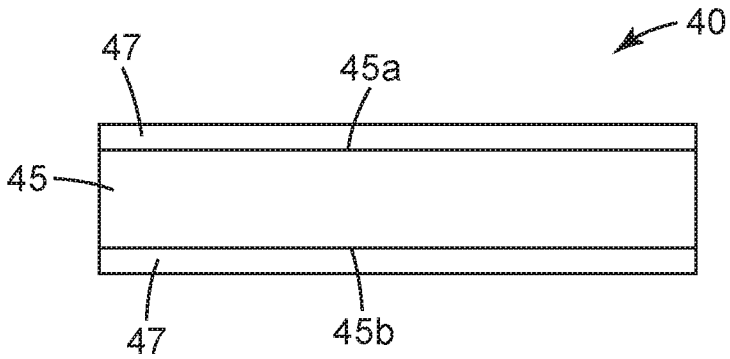

40
47
45a
45
47
45b

*Fig. 2*

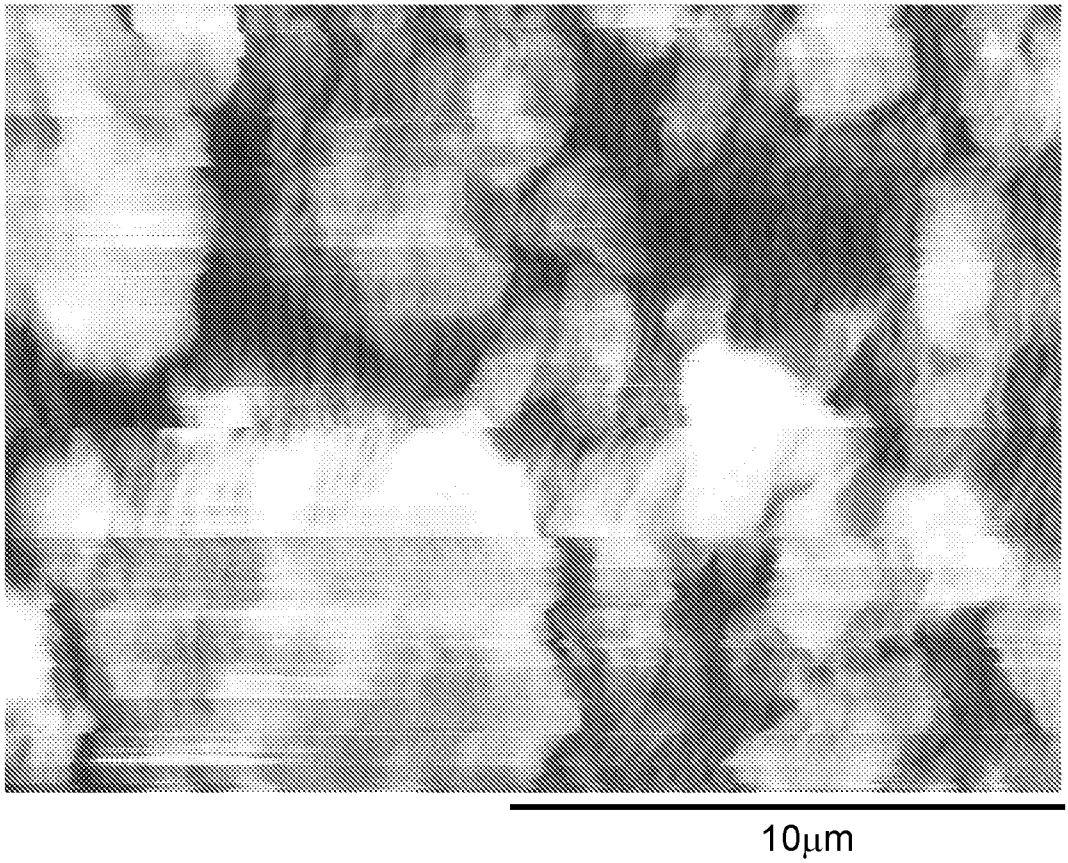

10μm

*Fig. 3*

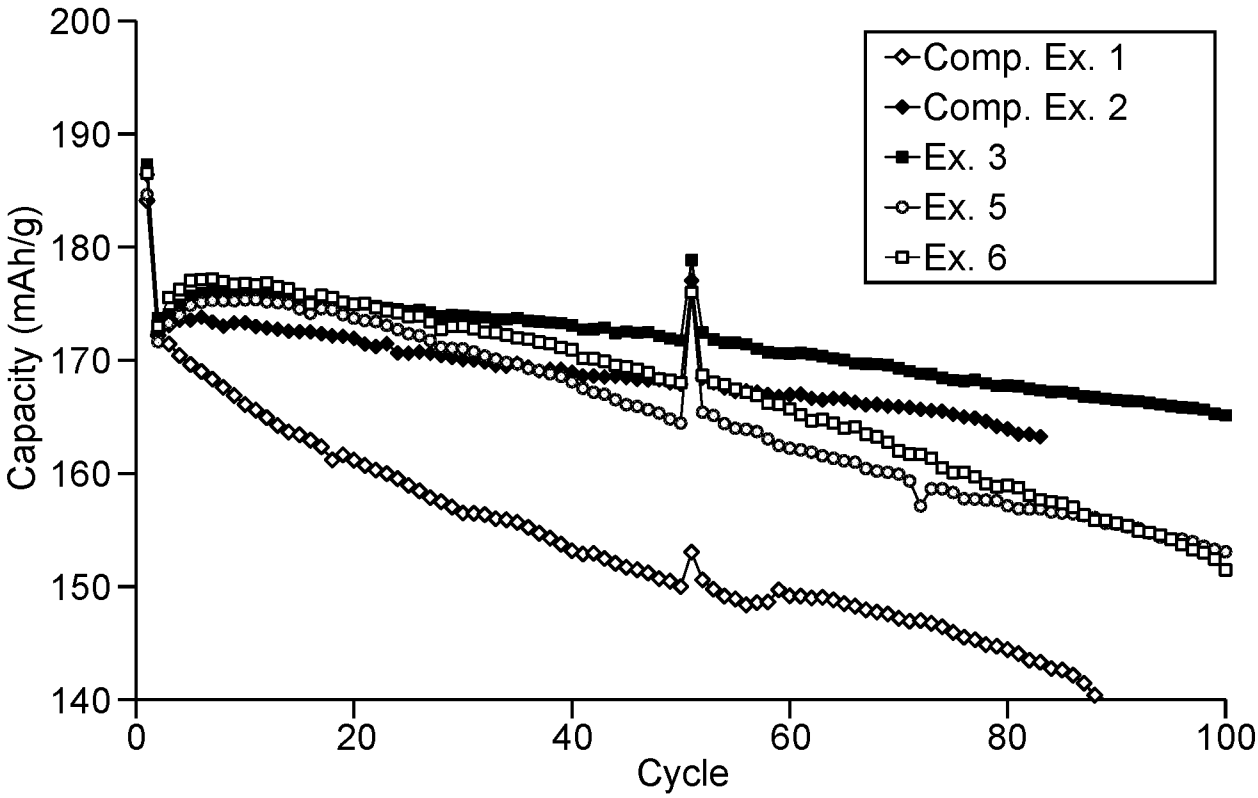

Comp. Ex. 1
Comp. Ex. 2
Ex. 3
Ex. 5
Ex. 6
Capacity (mAh/g)
200
190
180
170
160
150
140
0
20
40
60
80
100
Cycle

*Fig. 4*

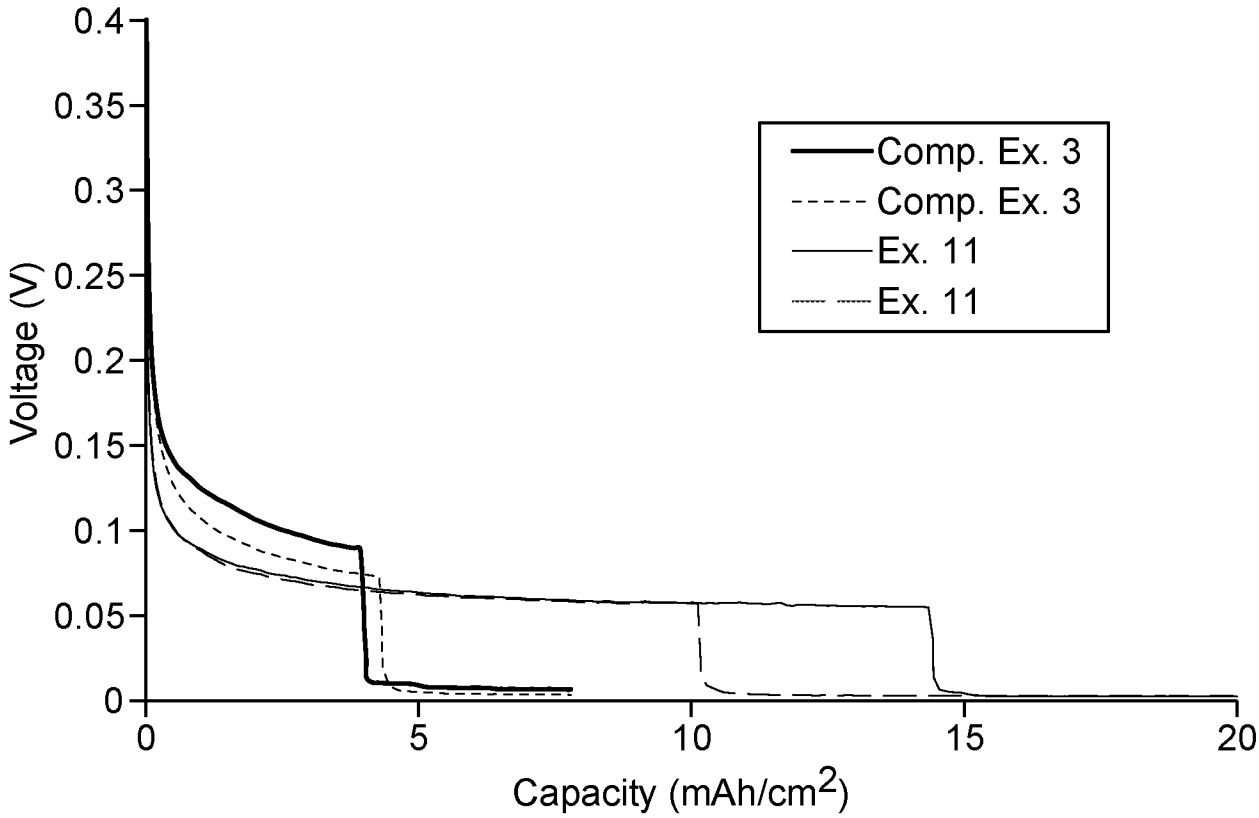

0.4
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
Voltage (V)
0
5
10
15
20
Capacity (mAh/cm2)
Comp. Ex. 3
Comp. Ex. 3
Ex. 11
Ex. 11

*Fig. 5*

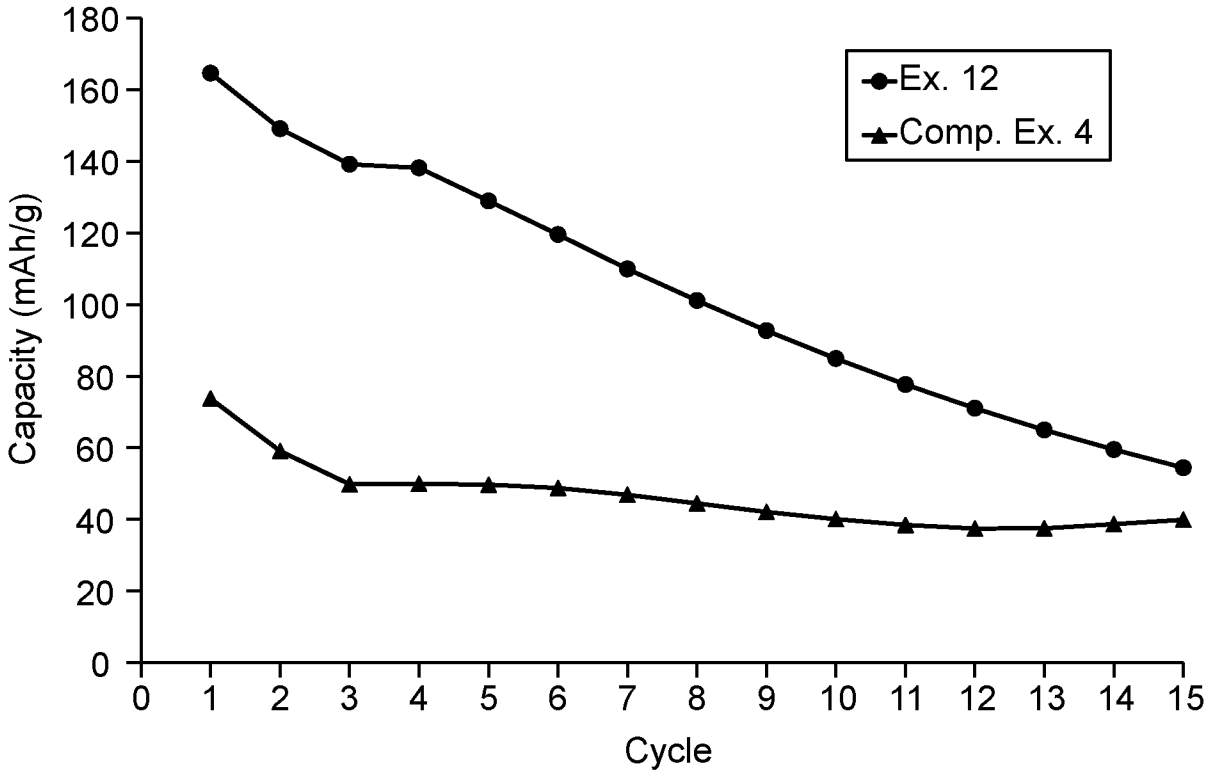

180
160
140
120
100
80
60
40
20
0
Capacity (mAh/g)
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
Cycle
Ex. 12
Comp. Ex. 4

*Fig. 6*

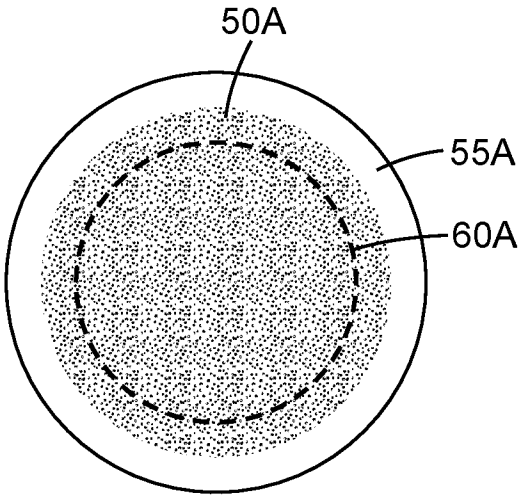



*Fig. 7A*

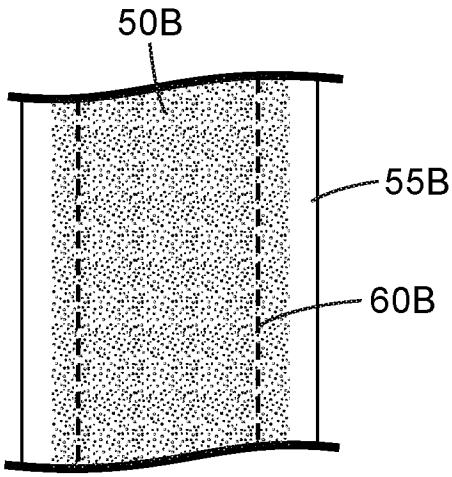



*Fig. 7B*

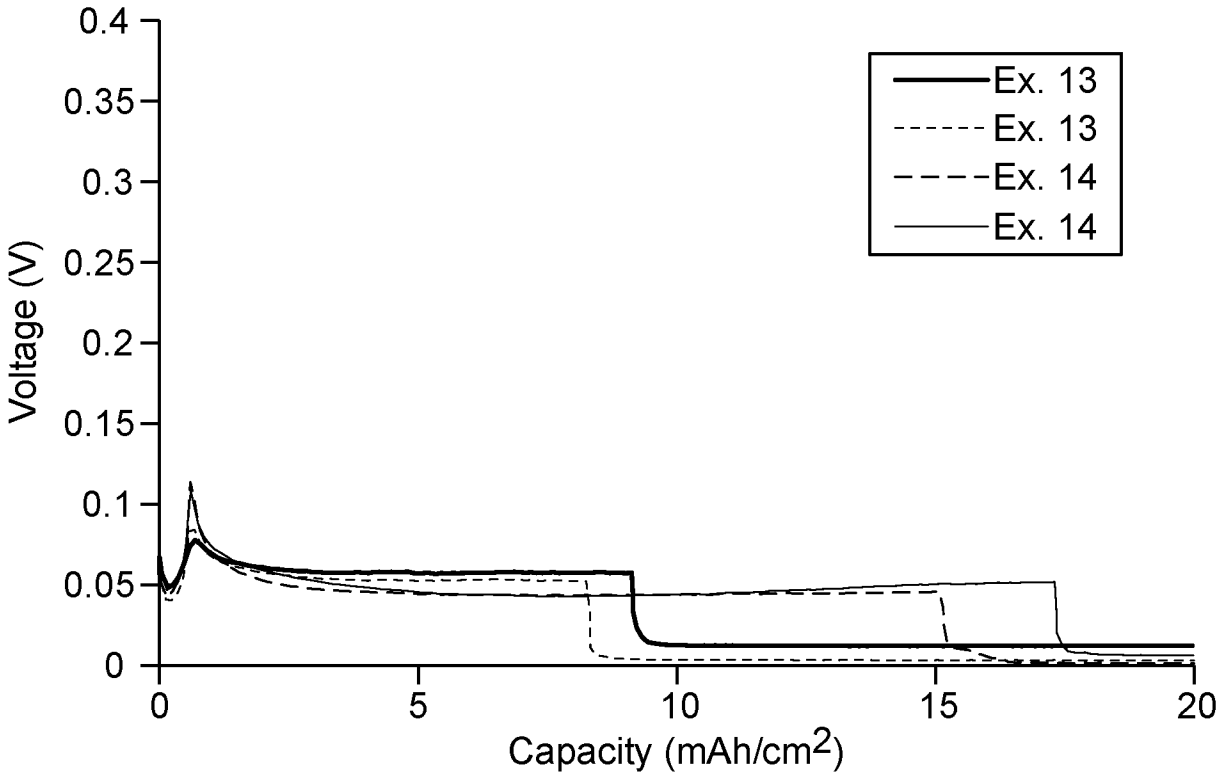



*Fig. 8*

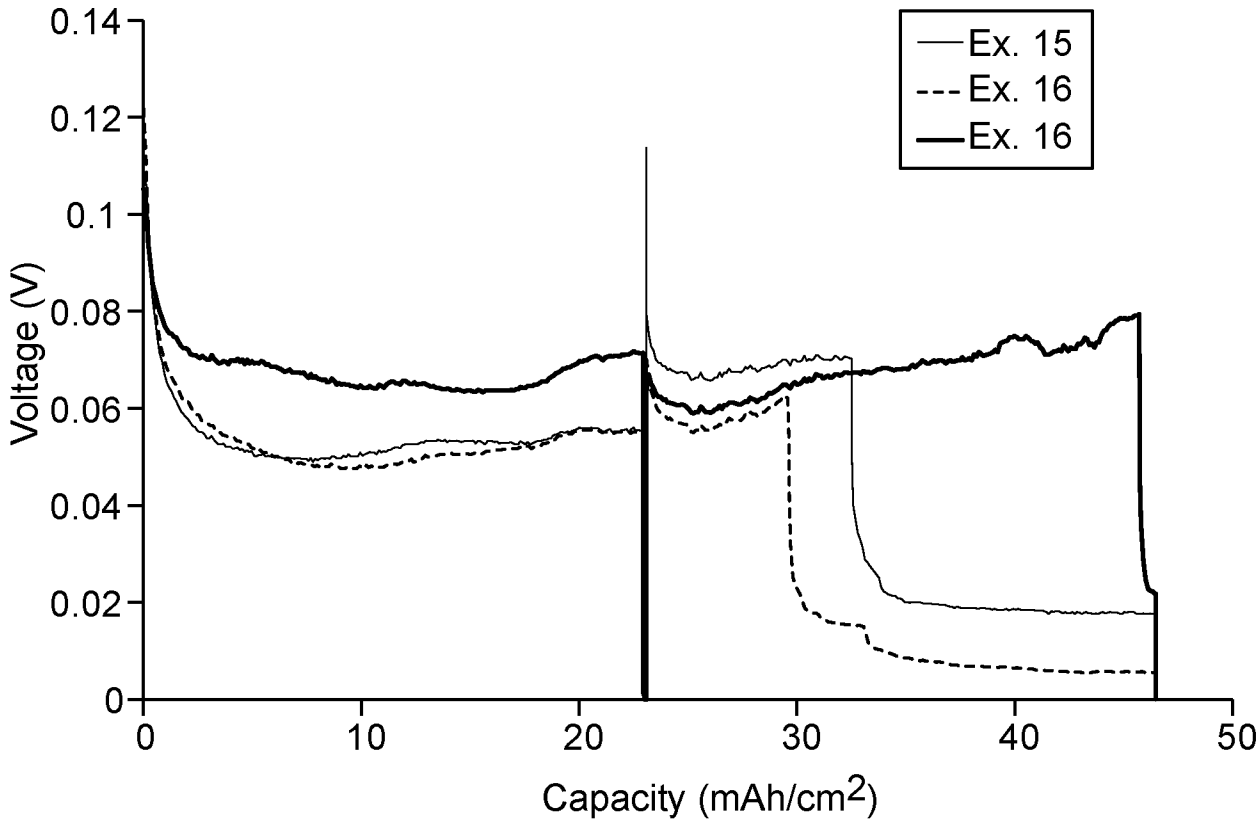

0.14
0.12
0.1
0.08
0.06
0.04
0.02
0
Voltage (V)
0
10
20
30
40
50
Capacity (mAh/cm2)
Ex. 15
Ex. 16
Ex. 16

*Fig. 9*

Comp. Ex. 5

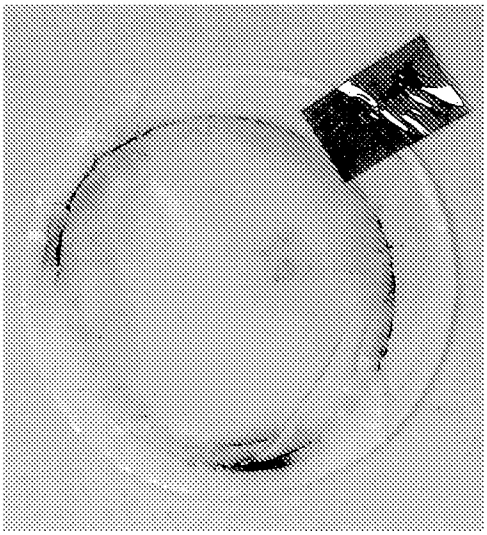


*Fig. 10A*

Comp. Ex. 6

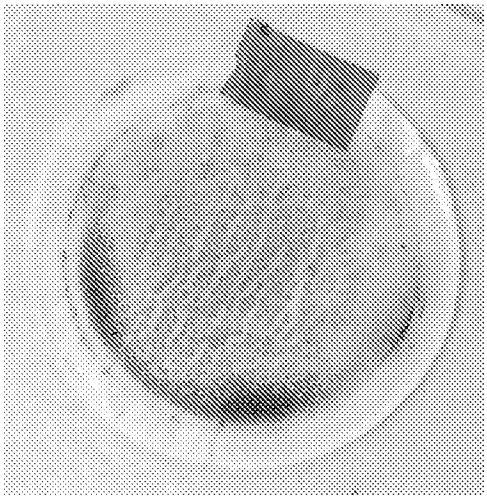


*Fig. 10B*

Ex. 17

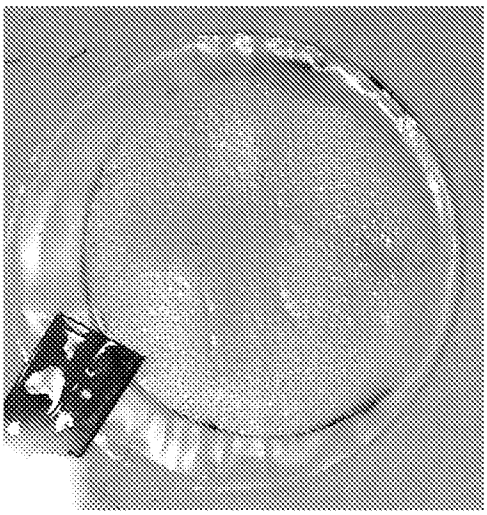


*Fig. 10C*

Ex. 18

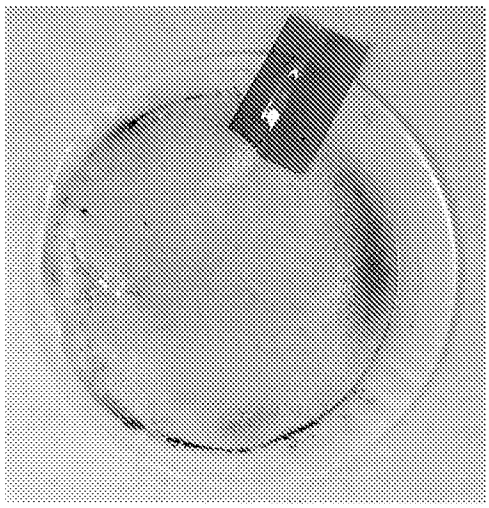


*Fig. 10D*

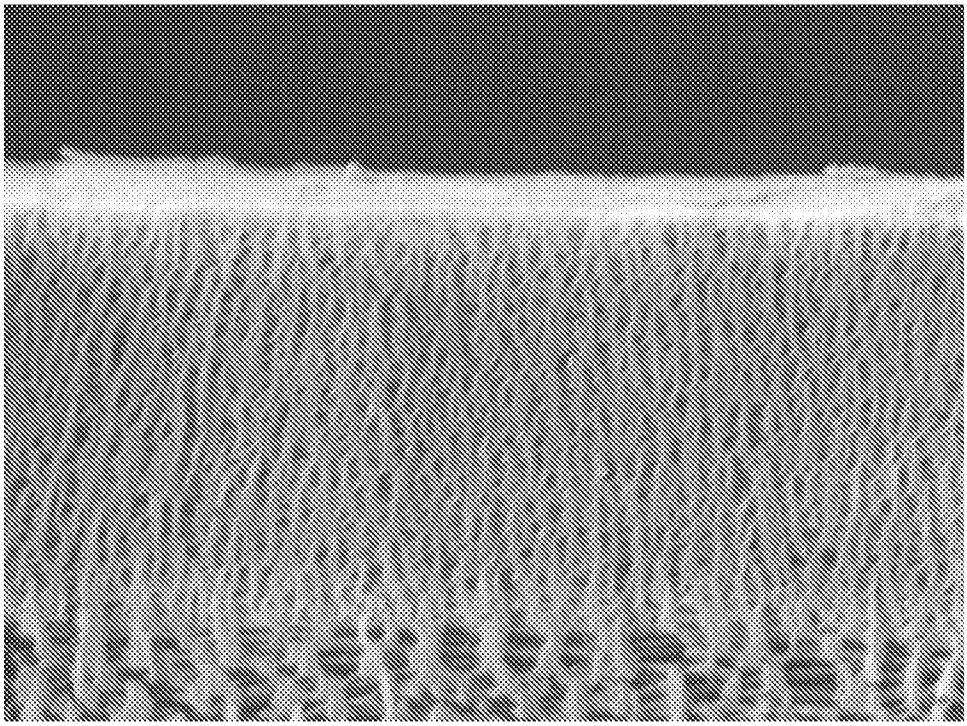



*Fig. 11*

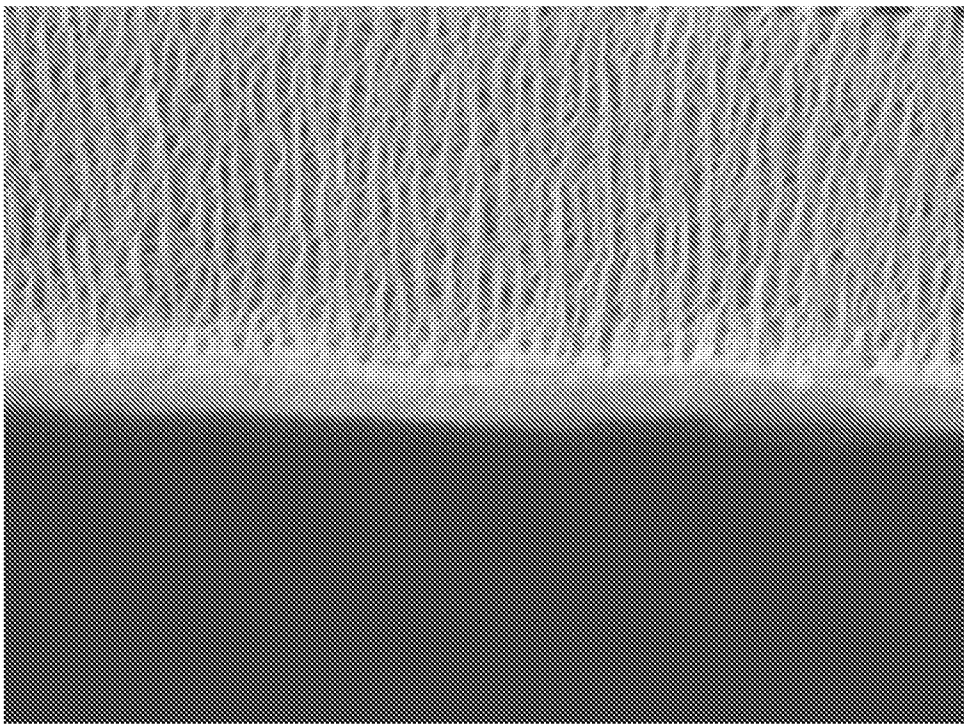



*Fig. 12*

# INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2017/022388

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - H01M 10/0525; B24B 1/00; B32B 9/04; B32B 15/04; H01G 11/04; H01G 11/22 (2017.01)

CPC - H01M 2/1686; B05D 5/12; B24B 1/00; B82B 3/00; C23C 24/02; H01G 9/045; H01G 11/04; H01G 11/42; H01G 11/70; H01G 11/86; H01M 2/145; H01M 2/1646; H01M 2/1653; H01M 4/0402; H01M 4/133; H01M 4/1393; H01M 4/661; H01M 10/052 (2017.02)

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)

See Search History document

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

See Search History document

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

See Search History document

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| Y | US 2012/0231321 A1 (HUANG et al) 13 September 2012 (13.09.2012) entire document | 1-16 |
| Y | US 2015/0024248 A1 (HE et al) 22 January 2015 (22.01.2015) entire document | 1-16 |
| Y | US 8,501,307 B2 (ZHAMU et al) 06 August 2013 (06.08.2013) entire document | 1-16 |
| Y | WO 2014/055258 A1 (MOMENTIVE PERFORMANCE MATERIALS INC. et al) 10 April 2014 (10.04.2014) entire document | 5, 16 |

☐ 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 |
|---|---|
| 01 May 2017 | 23 MAY 2017 |
| Name and mailing address of the ISA/US<br>Mail Stop PCT, Attn: ISA/US, Commissioner for Patents<br>P.O. Box 1450, Alexandria, VA 22313-1450<br>Facsimile No. 571-273-8300 | Authorized officer<br>Blaine R. Copenheaver<br>PCT Helpdesk: 571-272-4300<br>PCT OSP: 571-272-7774 |