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(54) SEPARATORS FOR ELECTROCHEMICAL CELLS

(71) Applicants: **Optodot Corporation**, Watertown, MA (US); **Sihl GmbH**, Duren (DE)

(72) Inventors: **Zhong Xu**, Holden, MA (US); **Steven A. Carlson**, Cambridge, MA (US)

(73) Assignees: **Sihl GmbH**, Duren (DE); **Optodot Corporation**, Watertown, MA (US)

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(57) ABSTRACT

Provided are separators for use in batteries and capacitors comprising (a) at least 50% by weight of an aluminum oxide and (b) an organic polymer, wherein the aluminum oxide is surface modified by treatment with an organic acid to form a modified aluminum oxide, and wherein the treatment provides dispersibility of the aluminum oxide in aprotic solvents such as N-methyl pyrrolidone. Preferably, the organic acid is a sulfonic acid, such as p-toluenesulfonic acid. Also preferably, the organic polymer is a fluorinated polymer, such as polyvinylidene fluoride. Also provided are electrochemical cells and capacitors comprising such separators.

SEPARATORS FOR ELECTROCHEMICAL CELLS

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application is a continuation of International Application Ser. No. PCT/US2011/001274, filed Jul. 18, 2011, which claims the benefit of U.S. provisional patent application Ser. No. 61/399,883, filed Jul. 19, 2010, the entirety of each which is hereby incorporated by reference.

FIELD OF THE INVENTION

[0002] The present invention relates generally to the field of porous membranes and to the fields of electric current producing cells and of separators for use in electric current producing cells. More particularly, this invention pertains to a porous separator membrane comprising an aluminum oxide and an organic polymer where the aluminum oxide has been surface modified by treatment with an organic acid to provide dispersibility in aprotic organic solvents. Also, the present invention pertains to electric current producing cells, such as lithium ion cells and capacitors, comprising such porous separators.

BACKGROUND

[0003] An electroactive material that has been fabricated into a structure for use in an electrochemical cell is referred to as an electrode. Of a pair of electrodes used in an electrochemical cell, the electrode on the electrochemically higher potential side is referred to as the positive electrode or the cathode, while the electrode on the electrochemically lower potential side is referred to as the negative electrode, or the anode. A battery may contain one or more electrochemical cells.

[0004] To prevent the undesirable flow of the electrons in a short circuit internally from the anode to the cathode, an electrolyte element is interposed between the cathode and the anode. This electrolyte element must be electronically nonconductive to prevent short circuits, but must permit the transport of ions between the anode and the cathode. The electrolyte element should also be stable electrochemically and chemically toward both the anode and the cathode.

[0005] Typically, the electrolyte element contains a porous material, referred to as a separator (since it separates or insulates the anode and the cathode from each other), and an aqueous or non-aqueous electrolyte, that usually comprises an ionic electrolyte salt and ionically conductive material, in the pores of the separator. A variety of materials have been used for the porous layer or separator of the electrolyte element in electrochemical cells. These porous separator materials include polyolefins such as polyethylenes and polypropylenes, glass fiber filter papers, and ceramic materials. Usually these separator materials are supplied as porous freestanding membranes that are interleaved with the anodes and the cathodes in the fabrication of electrochemical cells.

[0006] A liquid organic electrolyte containing organic solvents and lithium salts is typically used as the electrolyte in the pores of the separator in the electrolyte element for rechargeable or secondary lithium ion and non-rechargeable or primary lithium electrochemical cells. Alternatively, a gel or solid polymer electrolyte containing an ionically conductive polymer and lithium salts, and optionally organic solvents, might be utilized instead of the liquid organic electrolyte.

[0007] In addition to being porous and chemically stable to the other materials of the electric current producing cell, the separator should be flexible, thin, economical in cost, and have good mechanical strength and safety properties.

[0008] High porosity in the separator is important for obtaining the high ionic conductivity needed for effective performance in most batteries, except, for example, those batteries operating at relatively low charge and discharge rates, and for efficiency in capacitors, such as supercapacitors. It is desirable for the separator to have a porosity of at least 30 percent, and preferably 40 percent or higher, in lithium ion batteries.

[0009] Another highly desirable feature of the separator in the electrolyte element is that it is readily wetted by the electrolyte materials that provide the ionic conductivity. When the separator material is a polyolefin material that has non-polar surface properties, the electrolyte materials (which typically have highly polar properties) often poorly wet the separator material. This results in longer times to fill the battery with electrolyte and potentially in low capacities in the battery due to a non-uniform distribution of electrolyte materials in the electrolyte element.

[0010] The separators used for lithium ion batteries are typically polyolefin separators, which melt at below 200° C. and are very flammable. The lithium ion batteries, as well as lithium primary batteries and some capacitors, utilize highly flammable organic solvents in their electrolytes. A non-melting and flame retardant separator would help prevent the spread of any burning of the organic electrolyte, caused by an internal short circuit, thermal runaway, or other unsafe condition, that might spread into a larger area of the battery or capacitor and cause a major explosion. As lithium ion batteries are increasingly utilized for high power applications, such as for electric vehicles, the need for improved safety is greatly increased because of the very large size and high power rates of these vehicle batteries.

[0011] A separator that is applicable for lithium ion and other electric current producing cells and that has flame retardant and non-melting properties that provide safety against internal short shorts and thermal runaway, while maintaining the chemical stability of the electrolyte and of the separator, would be of great value to the battery and capacitor industry.

SUMMARY OF THE INVENTION

[0012] To achieve increased safety in separators for use in electric current producing cells such as batteries and capacitors, the present invention utilizes non-flammable inorganic oxides, such as aluminum oxides, and preferably non-flammable organic polymers having fluorinated groups in the separators. This invention utilizes various inorganic oxide particle pretreatment, mixing, coating, drying, and delaminating methods for preparing such separators.

[0013] One aspect of the present invention pertains to a separator for an electric current producing cell, wherein the separator comprises a microporous layer comprising (a) at least 50% by weight of an aluminum oxide and (b) an organic polymer, wherein the aluminum oxide is surface modified by treatment with an organic acid to form a modified aluminum oxide. In one embodiment, the organic acid is a sulfonic acid, preferably an aryl sulfonic acid, and more preferably a toluenesulfonic acid. In one embodiment, the organic acid is a carboxylic acid. In one embodiment, the aluminum oxide comprises a hydrated aluminum oxide of the formula $Al_2O_3 \cdot xH_2O$, wherein x is in the range of 1.0 to 1.5, and wherein the hydrated aluminum oxide is surface modified by treatment with an organic acid to form a modified hydrated aluminum oxide. In one embodiment, the modified aluminum oxide has an Al_2O_3 content in the range of 50 to 85% by weight. In one embodiment, the modified aluminum oxide has an Al_2O_3 content in the range of 65 to 80% by weight. In one embodiment, the separator comprises 60 to 90% by weight of the modified aluminum oxide. In one embodiment, the separator comprises 70 to 85% by weight of the modified aluminum oxide. In one embodiment, the microporous layer is a xerogel layer. In one embodiment, the organic polymer comprises a polyvinylidene fluoride polymer. In one embodiment, the separator comprises a copolymer of a first fluorinated organic monomer and a second organic monomer. In one embodiment, the second organic monomer is a second fluorinated organic monomer.

[0014] In one embodiment of the separators of this invention, the electric current producing cell is a secondary lithium ion cell. In one embodiment, the electric current producing cell is a primary lithium cell. In one embodiment, the electric current producing cell is a capacitor. In one embodiment, the separator does not melt at temperatures lower than 300° C. In one embodiment, the separator is a flame retardant separator.

[0015] Another aspect of the present invention pertains to an electrochemical cell comprising an anode, a cathode, an organic electrolyte comprising a lithium salt, and a separator interposed between the anode and the cathode, wherein the separator comprises a microporous layer comprising (a) at least 50% by weight of an aluminum oxide and (b) an organic polymer, wherein the aluminum oxide is surface modified by treatment with an organic acid. In one embodiment, the organic acid is a sulfonic acid, preferably an aryl sulfonic acid, and more preferably a toluenesulfonic acid. In one embodiment, the organic acid is a carboxylic acid. In one embodiment, the aluminum oxide comprises a hydrated aluminum oxide of the formula $Al_2O_3 \cdot xH_2O$, wherein x is in the range of 1.0 to 1.5, and wherein the hydrated aluminum oxide is surface modified by treatment with an organic acid to form a modified hydrated aluminum oxide.

[0016] In one embodiment of the electrochemical cells of this invention, the microporous layer is a xerogel layer. In one embodiment, the anode active material of the anode is lithium. In one embodiment, the modified aluminum oxide has an Al_2O_3 content in the range of 50 to 85% by weight. In one embodiment, the modified aluminum oxide has an Al_2O_3 content in the range of 65 to 80% by weight. In one embodiment, the organic polymer comprises a polyvinylidene fluoride polymer. In one embodiment, the organic polymer comprises a copolymer of a first fluorinated organic monomer and a second organic monomer. In one embodiment, the second organic monomer is a second fluorinated organic monomer. In one embodiment, the lithium salt is lithium hexafluorophosphate.

[0017] Another aspect of the present invention relates to a capacitor comprising two electrodes, an organic electrolyte comprising a tetraalkyl ammonium salt, and a separator interposed between the two electrodes, wherein the separator comprises a microporous layer comprising (a) at least 50% by weight of an aluminum oxide and (b) an organic polymer, wherein the aluminum oxide is surface modified by treatment with an organic acid to form a modified aluminum oxide. In one embodiment, the inorganic oxide comprises a hydrated aluminum oxide of the formula $Al_2O_3 \cdot xH_2O$ wherein x is in the range of 1.0 to 1.5, wherein the aluminum oxide is surface modified by treatment with an organic acid to form a modified aluminum oxide. In one embodiment, the organic acid is a sulfonic acid. In one embodiment, the microporous layer is a xerogel layer. In one embodiment, the organic polymer comprises a polyvinylidene fluoride polymer. In one embodiment, the organic polymer comprises a copolymer of a first fluorinated organic monomer and a second organic monomer.

DETAILED DESCRIPTION OF THE INVENTION

[0018] The separators of the present invention provide superior safety and other key performance properties for use in electric current producing cells, including, but not limited to, lithium batteries and capacitors. Methods of preparing microporous xerogel separators for electrochemical cells are described in U.S. Pat. Nos. 6,153,337 and 6,306,545, and in U.S. Pat. Application 20020092155, all to Carlson et al. The liquid mixture described in these references for coating xerogel separators comprises an inorganic oxide, an organic binder, and typically water as the volatile liquid in the mixture. Optionally, the liquid mixture comprises organic solvents, preferably protic organic solvents. Examples of protic organic solvents are alcohols and glycols.

[0019] The drying process to form a xerogel layer involves the removal of the liquid in the liquid mixture. As is known in the art of inorganic oxide xerogel coatings, as the liquid is removed, the colloidal particles of inorganic oxide sol form a gel that, upon further loss of liquid, forms a 3-dimensional microporous network of inorganic oxide. By the terms "xerogel layer" and "xerogel structure," as used herein, is meant, respectively, a layer of a coating or the structure of a coating layer in which the layer and structure were formed by drying a liquid sol or sol-gel mixture to form a solid gel matrix as, for example, described in *Chem. Mater.*, Vol. 9, pages 1296 to 1298 (1997) by Ichinose et al. for coating layers of inorganic oxide based xerogels. Thus, if the liquid of the gel formed in the liquid sol-gel mixture is removed substantially, for example, through the formation of a liquid-vapor boundary phase, the resulting gel layer or film is termed, as used herein, a xerogel layer. Thus, the microporous xerogel layers of this invention comprise a dried microporous three-dimensional solid network with pores which are interconnected in a substantially continuous fashion from one outermost surface of the layer through to the other outermost surface of the layer. A continuous xerogel coating layer has the materials of the xerogel in a continuous structure in the coating layer, i.e., the materials, such as inorganic oxide particles, are in contact and do not have discontinuities in the structure, such as a discontinuous layer of solid pigment particles that are separated from each other.

[0020] In contrast, xerogel pigment particles may be formed by a xerogel process involving drying a liquid solution of a suitable precursor to the pigment to form a dried mass of xerogel pigment particles, which is typically then ground to a fine powder to provide xerogel pigment particles. The microporous inorganic oxide layers of this invention may be, but are not limited to, xerogel layers. The inorganic oxide layers of the present invention may also be discontinuous layers of solid pigment particles that are not a xerogel coating layer and have discontinuities of solid pigment particles that are separated from each other in the structure of the discontinuous layer. This separation typically involves organic polymer interposed between the pigment particles. The terms "xerogel coating" and "xerogel coating layer," as used herein, are synonymous with the term "xerogel layer."

[0021] As used herein, the term "microporous" describes the material of a layer or coating, in which the material possesses pores of a diameter of about 1 micron or less. As used herein, the term "nanoporous" describes the material of a layer or coating, in which the material possesses pores of a diameter of about 100 nanometers or less.

[0022] Preferably for battery and capacitor separator applications, these pores are connected in a substantially continuous fashion from one outermost surface of the microporous layer through to the other outermost surface of the layer. This substantially continuous 3-dimensional microporous inorganic oxide network is efficient in allowing the diffusion of ions, such as lithium ions, through the separator during the charging and discharging of the electric current producing cell.

[0023] The amount of the pores in the separator may be characterized by the percent porosity or percent pore volume, which is the cubic centimeters of pores per cubic centimeters of the separator. The porosity may be measured by filling the pores with a relatively non-volatile liquid having a known density and then calculated by the increase in weight of the separator with the liquid present divided by the known density of the liquid and then dividing this quotient by the volume of the separator, as calculated from the area and average thickness of the separator.

[0024] In one embodiment of the separators of this invention, the average pore diameter of the microporous inorganic oxide layer is from 2 nm to 70 nm. Typically, the average pore diameter of the microporous inorganic oxide layer is from 30 to 50 nm. These extremely small pores, that are about 5 to 10 times smaller than the average pore dimensions of polyolefin separators, present no limitation to high conductivity with lithium salt electrolytes. Thus, the pore sizes of the separators of this invention may provide ion transport and conductivity with lithium ion battery electrolytes that is at least equal to that of polyolefin separators.

[0025] In one embodiment of the separators of this invention, the inorganic oxide is an aluminum oxide. Other inorganic oxides, such as zirconium oxides and silicas, as known in the art of electrolyte elements and separators for electrochemical cells, may be utilized alone or in combination with other inorganic oxides including aluminum oxides. Preferred aluminum oxides are aluminum boehmites. The term "pseudo-boehmite," as used herein, pertains to hydrated aluminum oxides having the chemical formula, $Al_2O_3 \cdot xH_2O$, wherein x is in the range of 1.0 to 1.5. Terms used herein, which are synonymous with "pseudo-boehmite," include "aluminum boehmite," "boehmite," "AlOOH," and "hydrated alumina." The materials referred to herein as "pseudo-boehmite" are distinct from anhydrous aluminum oxides or aluminas (Al_2O_3 such as alpha-alumina or gamma-alumina) and hydrated aluminum oxides of the formula $Al_2O_3 \cdot xH_2O$ wherein x is less than 1.0 or greater than 1.5. In one embodiment of the separators of the present invention, the weight percent of the aluminum oxide in the separator is greater than 50%. This loading of the aluminum oxide helps to provide the porosity of the separator that is needed for conductivity and for rapid wetting by the electrolyte when manufacturing the electric current producing cell.

[0026] One aspect of the present invention pertains to a separator for an electric current producing cell, wherein the separator comprises a microporous layer comprising (a) at least 50% by weight of an aluminum oxide and (b) an organic polymer, wherein the aluminum oxide is surface modified by treatment with an organic acid to form a modified aluminum oxide. The separator may contain only the microporous layer of this invention or may contain additional microporous layers, such as porous polyolefin layers as typically used in lithium ion batteries. For example, the microporous layer of the present invention may be coated on one or both sides of a microporous polyolefin layer, such as Celgard 2500, the trade name for a polyolefin separator membrane available from Polypore, Inc., of Charlotte, N.C.. Whereas a thickness of 5 to 20 microns is typical for the separators of this invention that contain only the microporous layers of this invention, the thickness of a coating of the microporous layer of this invention onto a polyolefin microporous separator is typically in, but not limited to, the range of 1 to 4 microns.

[0027] In one embodiment of the separators of the present invention, the organic acid is a sulfonic acid, preferably an aryl sulfonic acid, and more preferably a toluenesulfonic acid. In one embodiment, the organic acid is a carboxylic acid. One purpose of the surface modification of the aluminum oxide is to make the aluminum oxide particles dispersible in organic solvents, especially in aprotic organic solvents. This broader scope of dispersibility is advantageous in enabling a wider range of organic polymers that are soluble in aprotic organic solvents, but not in water and alcohols, to be used. Other types of surface modification of inorganic oxides, as known in the art of surface modification of inorganic oxides for excellent dispersibility in aprotic organic solvents may be utilized in the present invention.

[0028] In one embodiment of the separators of this invention, the aluminum oxide comprises a hydrated aluminum oxide of the formula $Al_2O_3 \cdot xH_2O$, wherein x is in the range of 1.0 to 1.5, and wherein the hydrated aluminum oxide is surface modified by treatment with an organic acid to form a modified hydrated aluminum oxide. In one embodiment, the modified aluminum oxide has an Al_2O_3 content in the range of 50 to 85% by weight. In one embodiment, the modified aluminum oxide has an Al_2O_3 content in the range of 65 to 80% by weight. In one embodiment, the separator comprises 60 to 90% by weight of the modified aluminum oxide. In one embodiment, the separator comprises 70 to 85% by weight of the modified aluminum oxide. In one embodiment, the microporous layer is a xerogel layer. In one embodiment, the organic polymer comprises a polyvinylidene fluoride (PVDF) polymer, such as KYNAR HSV 900, the trade name for a PVDF polymer for lithium battery and other applications available from Arkema, Inc. In one embodiment, the separator comprises a copolymer of a first fluorinated organic monomer and a second organic monomer. In one embodiment, the second organic monomer is a second fluorinated organic monomer.

[0029] In one embodiment of the separators of this invention, the electric current producing cell is a secondary lithium ion cell. In one embodiment, the electric current producing cell is a primary lithium cell. In one embodiment, the electric current producing cell is a capacitor. In one embodiment, the separator does not melt at temperatures lower than 300° C. The aluminum oxide or other inorganic oxide material is primarily responsible for providing this non-melting and dimensionally stable property at high temperatures. In one embodiment, the separator is a flame retardant separator. The aluminum oxide or other inorganic oxide is a flame retardant material and, in combination with a highly fluorinated organic polymer which is also flame retardant, provides a flame retardant separator.

[0030] Another aspect of the present invention pertains to an electrochemical cell comprising an anode, a cathode, an organic electrolyte comprising a lithium salt, and a separator interposed between the anode and the cathode, wherein the separator comprises a microporous layer comprising (a) at least 50% by weight of an aluminum oxide and (b) an organic polymer, wherein the aluminum oxide is surface modified by treatment with an organic acid. In one embodiment, the organic acid is a sulfonic acid, preferably an aryl sulfonic acid, and more preferably a toluenesulfonic acid. In one embodiment, the organic acid is a carboxylic acid. In one embodiment, the aluminum oxide comprises a hydrated aluminum oxide of the formula $Al_2O_3 \cdot xH_2O$, wherein x is in the range of 1.0 to 1.5, and wherein the hydrated aluminum oxide is surface modified by treatment with an organic acid to form a modified hydrated aluminum oxide.

[0031] In one embodiment of the electrochemical cells of this invention, the microporous layer is a xerogel layer. In one embodiment, the anode active material of the anode is lithium. In one embodiment, the modified aluminum oxide has an Al_2O_3 content in the range of 50 to 85% by weight. In one embodiment, the modified aluminum oxide has an Al_2O_3 content in the range of 65 to 80% by weight. In one embodiment, the organic polymer comprises a polyvinylidene fluoride polymer. In one embodiment, the organic polymer comprises a copolymer of a first fluorinated organic monomer and a second organic monomer. In one embodiment, the second organic monomer is a second fluorinated organic monomer. In one embodiment, the lithium salt is lithium hexafluorophosphate.

[0032] Another aspect of the present invention relates to a capacitor comprising two electrodes, an organic electrolyte comprising a tetraalkyl ammonium salt, and a separator interposed between the two electrodes, wherein the separator comprises a microporous layer comprising (a) at least 50% by weight of an aluminum oxide and (b) an organic polymer, wherein the aluminum oxide is surface modified by treatment with an organic acid to form a modified aluminum oxide. In one embodiment, the inorganic oxide comprises a hydrated aluminum oxide of the formula $Al_2O_3 \cdot xH_2O$ wherein x is in the range of 1.0 to 1.5, wherein the aluminum oxide is surface modified by treatment with an organic acid to form a modified aluminum oxide. In one embodiment, the organic acid is a sulfonic acid. In one embodiment, the microporous layer is a xerogel layer. In one embodiment, the organic polymer comprises a polyvinylidene fluoride polymer. In one embodiment, the organic polymer comprises a copolymer of a first fluorinated organic monomer and a second organic monomer.

EXAMPLES

[0033] Several embodiments of the present invention are described in the following examples, which are offered by way of illustration and not by way of limitation.

Example 1

[0034] A 20% by weight dispersion of DISPAL 10SR, the trade name for a surface-modified aluminum oxide available from SASOL North America, Houston, Tex., in methyl ethyl ketone was prepared. According to the Material Safety Data Sheet (MSDS) by SASOL for DISPAL 10SR, the aluminum oxide is an aluminum boehmite, and the surface modification comprises p-toluenesulfonic acid (PTSA). Separately, a 10% by weight solution of KYNAR HSV 900 in N-methyl pyrrolidone (NMP) was prepared. The aluminum oxide dispersion was added to the stirred fluoropolymer solution to prepare a dispersion containing the aluminum oxide and fluoropolymer in a dry weight ratio of 5:1. The % solids of this dispersion was about 17%.

[0035] This dispersion was coated onto a 3 mil thick silicone treated polyester (PET) film on the silicone release side to give a dry coating thickness of about 20 microns and then delaminated from the release substrate to provide a free standing aluminum oxide microporous separator with a porosity of about 43%. Evaluation of this aluminum oxide microporous separator in a typical lithium ion button cell with a graphite-containing anode, a lithium hexfluorophosphate-containing electrolyte in organic carbonate solvents, and a cobalt oxide-containing cathode showed equal or better chemical stability at 55° C., cycling, and ionic conductivity at 1C and 5C charge, in comparison to a control button cell with an Ube polyolefin separator of the same thickness substituted for the aluminum oxide separator.

[0036] The aluminum oxide separator did not melt at temperatures below 300° C. and was flame retardant, as shown by not burning when exposed to an open flame.

Example 2

[0037] The aluminum oxide and fluoropolymer dispersion of Example 1 was coated onto a 20 micron thick polyolefin separator from Ube and dried at 90° C. to avoid shrinkage and melting of the polyolefin separator. The thickness of the coating was varied from 1 to 4 microns dry and coated on one or both sides of the polyolefin separator. Button cells as described in Example 1 were prepared with a 2 micron thick aluminum oxide microporous coating on one or both sides of the polyolefin separator and gave comparable stability at 55° C., cycling, and conductivity to control button cells with the polyolefin separator only.

Comparative Example 1

[0038] A 20% by weight dispersion of DISPAL 10F4, the trade name for a surface-modified aluminum boehmite available from SASOL North America, Houston, Tex., in methyl ethyl ketone was mixed at 2200 rpm stirring for 40 minutes. No satisfactory dispersion was obtained, and nearly all of the pigment settled to the bottom of the mix container. According to the Material Safety Data Sheet (MSDS) by SASOL for DISPAL 10F4, the surface modification comprises formic acid. Separately, a 10% by weight solution of KYNAR HSV 900 in NMP was prepared. The non-dispersed DISPAL 10F4 mix in methyl ethyl ketone was added to the stirred fluoropolymer solution at a dry weight ratio of 3:1 of the aluminum boehmite and fluoropolymer with continued stirring at 2200 rpm for 40 minutes. No satisfactory dispersion was obtained, and nearly all of the pigment settled to the bottom of the mix container. The mix was not suitable for coating a separator layer on a release substrate.

Comparative Example 2

[0039] A 7.5% by weight solution of KYNAR HSV 900 in NMP was prepared. To this fluoropolymer solution with stirring at 2200 rpm, DISPAL 10F4 in a dry weight ratio of 5:1 of the aluminum boehmite and fluoropolymer was added slowly with continued stirring at 2200 rpm for 40 minutes. No satisfactory dispersion was obtained, and nearly all of the pigment settled to the bottom of the mix container. The mix was not suitable for coating a separator layer on a release substrate.

[0040] Comparative Examples 1 and 2 show that surface modification of an aluminum oxide with formic acid does not provide dispersibility in aprotic solvents as represented by NMP and methyl ethyl ketone and consequently is not suitable for coating separators with polyvinylidene fluoride (PVdF) and other fluoropolymers that require aprotic solvents such as NMP for solubility and for use in coatings, such as a separator or battery electrode coating.

[0041] While the invention 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

What is claimed is:

1. A separator for an electric current producing cell, wherein said separator comprises a microporous layer comprising (a) at least 50% by weight of an aluminum oxide and (b) an organic polymer, wherein said aluminum oxide is surface modified by treatment with an organic acid to form a modified aluminum oxide, and wherein said treatment provides dispersibility of said aluminum oxide in aprotic solvents, and said organic polymer comprises a first fluorinated organic monomer and a second organic monomer or said organic polymer comprises a polyvinylidene fluoride polymer.

2. The separator of claim **1**, wherein said organic acid is a sulfonic acid.

3. The separator of claim **2**, wherein said sulfonic acid is an aryl sulfonic acid, preferably a toluenesulfonic acid.

4. The separator of claim **1**, wherein said organic acid is a carboxylic acid.

5. The separator of claim **1**, wherein said aluminum oxide comprises a hydrated aluminum oxide of the formula $Al_2O_3 \cdot xH_2O$, wherein x is in the range of 1.0 to 1.5, and wherein said hydrated aluminum oxide is surface modified by treatment with an organic acid to form a modified hydrated aluminum oxide.

6. The separator of claim **5**, wherein said separator comprises 60 to 90% by weight of said modified aluminum oxide.

7. The separator of claim **5**, wherein said microporous layer has an average pore diameter from 2 nm to 70 nm.

8. The separator of claim **1**, wherein said electric current producing cell is a secondary lithium ion cell, a primary lithium cell, or a capacitor.

9. The separator of claim **1**, wherein said microporous layer is coated on one or both sides of at least one microporous polyolefin layer.

10. An electrochemical cell comprising an anode, a cathode, an organic electrolyte comprising a lithium salt, and a separator interposed between said anode and said cathode, wherein said separator comprises a microporous layer comprising (a) at least 50% by weight of an aluminum oxide and (b) an organic polymer, wherein said aluminum oxide is surface modified by treatment with an organic acid to form a modified aluminum oxide, and wherein said treatment provides dispersibility of said aluminum oxide in aprotic solvents, and said organic polymer comprises a first fluorinated organic monomer and a second organic monomer or said organic polymer comprises a polyvinylidene fluoride polymer.

11. The cell of claim **10**, wherein said organic acid is a sulfonic acid.

12. The cell of claim **11**, wherein said sulfonic acid is an aryl sulfonic acid, preferably a toluenesulfonic acid.

13. The cell of claim **10**, wherein said organic acid is a carboxylic acid.

14. The cell of claim **10**, wherein said aluminum oxide comprises a hydrated aluminum oxide of the formula $Al_2O_3xH_2O$, wherein x is in the range of 1.0 to 1.5, and wherein said hydrated aluminum oxide is surface modified by treatment with an organic acid to form a modified hydrated aluminum oxide.

15. The cell of claim **10**, wherein said microporous layer has an average pore diameter from 2 nm to 70 nm.

16. The cell of claim **10**, wherein said microporous layer is coated on one or both sides of at least one microporous polyolefin layer.

17. The cell of claim **10**, wherein the anode active material of said anode is lithium.

18. A capacitor comprising two electrodes, an organic electrolyte comprising a tetraalkyl ammonium salt, and a separator interposed between said two electrodes, wherein said separator comprises a microporous layer comprising (a) at least 50% by weight of an aluminum oxide and (b) an organic polymer, wherein said aluminum oxide is surface modified by treatment with an organic acid to form a modified aluminum oxide, and wherein said treatment provides dispersibility of said aluminum oxide in aprotic solvents, and said organic polymer comprises a first fluorinated organic monomer and a second organic monomer or said organic polymer comprises a polyvinylidene fluoride polymer.

19. The capacitor of claim **18**, wherein said organic acid is a sulfonic acid.

20. The capacitor of claim **18**, wherein said inorganic oxide comprises a hydrated aluminum oxide of the formula $Al_2O_3 \cdot xH_2O$, wherein x is in the range of 1.0 to 1.5, and wherein said aluminum oxide is surface modified by treatment with an organic acid to form a modified aluminum oxide.

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