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(54) ELECTRICALLY CONDUCTING ORGANIC POLYMER/NANOPARTICLE COMPOSITES AND METHODS FOR USE THEREOF

ELEKTRISCH LEITENDE ORGANISCHE POLYMER-/ NANOPARTIKELZUSAMMENSETZUNGEN UND VERWENDUNGSVERFAHREN DAFÜR

COMPOSITES POLYMERES/NANOPARTICULES ORGANIQUES ELECTROCONDUCTEURS ET PROCEDES D'UTILISATION ASSOCIES

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Description

Field of the Invention

[0001] The invention relates to the use of conductive organic polymers in the production of electronic devices.

Background

[0002] Conductive organic polymers originally attracted the attention of researchers over 20 years ago. The interest generated by these polymers compared to conventional conducting materials (e.g., metals, semiconductive metal oxides) was largely due to factors such as light weight, flexibility, durability, and potential ease of processing. To date the most commercially successful conductive organic polymers are the polyanilines and polythiophenes, which are marketed under a variety of tradenames. These materials can be prepared by polymerizing aniline or dioxythiophene monomers in aqueous solution in the presence of a water soluble polymeric acid, such as poly(styrenesulfonic acid) (PSS), as described in, for example, U.S. Patent No. 5,300,575 entitled "Polythiophene dispersions, their production and their use." The recent development of electroluminescent (EL) devices for use in light emissive displays and thin film field effect transistors for use as electrodes has resulted in a new area of interest in conductive organic polymers. EL devices such as organic light emitting diodes (OLEDs) containing conductive organic polymers generally have the following configuration:

anode/buffer layer/EL material/cathode

[0003] The anode is typically any material that has the ability to inject holes into the EL material, such as, for example, indium/tin oxide (ITO). The anode is optionally supported on a glass or plastic substrate. EL materials include fluorescent dyes, fluorescent and phosphorescent metal complexes, conjugated polymers, and mixtures thereof. The cathode is typically any material, such as Ca or Ba, that has the ability to inject electrons into the EL material.

[0004] The buffer layer is typically a conductive organic polymer which facilitates the injection of holes from the anode into the EL polymer layer. The buffer layer can also be called a hole-injection layer, a hole transport layer, or may be characterized as part of a bilayer anode. Typical aqueous-dispersible conductive organic polymers employed as buffer layers are the emeraldine salt form of polyaniline ("PAni") or a polymeric dioxyalkylenethiophene doped with a polymeric sulfonic acid.

[0005] While the buffer layer must have some electrical conductivity in order to facilitate charge transfer, the highest conductivity of buffer layer films derived from commonly known aqueous polyaniline or polythiophene dispersion is generally in the range of about 10^{-3} S/cm. The conductivity is about three order magnitude higher than necessary. Indeed, in order to prevent cross-talk between anode lines (or pixels), the electrical conductivity of the buffer layers should be minimized to about 10^{-6} S/cm without negatively affecting the light emitting properties of a device containing such a buffer layer. For example, a film made from a commercially available aqueous poly(ethylenedioxythiophene) ("PEDT") dispersion, Baytron®-P VP Al 4083 from H. C. Starck, GmbH, Leverkusen, Germany, has condutivity of $\sim 10^{-3}$ S/cm. This is too high to avoid cross-talk between pixels. Baytron® .P VP Al 4083 and Baytron® .P VP CH 8000 are described in the product information catalogue available from H.C. Stark Inc. published May 2001. Accordingly, there is a need for high resistance buffer layers for use in electroluminescent devices. There is also a need for improved properties for microelectronics applications.

SUMMARY OF THE INVENTION

[0006] New compositions are provided according to claim 1. The new compositions are capable of providing films in electronic devices.

[0007] The present invention also provides a method of making a buffer layer according to claim 8.

[0008] The foregoing general description and the following detailed description are exemplary and explanatory only and are not restrictive of the invention, as defined in the appended claims.

BRIEF DESCRIPTION OF THE DRAWINGS

[0009] The invention is illustrated by way of example and not limited in the accompanying figure.

[0010] FIG. 1 illustrates a cross-sectional view of an electronic device that includes a buffer layer comprising the new composition.

DETAILED DESCRIPTION

[0011] Compositions are provided comprising aqueous dispersions of at least one electrically conducting organic polymer and a plurality of at least one nanoparticle.

[0012] As used herein, the term "dispersion" refers to a continuous liquid medium containing a suspension of minute particles. The "continuous medium" comprises an aqueous liquid. As used herein, the term "aqueous" refers to a liquid that has a significant portion of water and in one embodiment it is at least about 40% by weight water. As used herein, the term "nanoparticles" refers to particles having sizes less than about 1000 nanometers (nm). Nanoparticles according to the new composition can be inorganic or organic. As used herein, the term "inorganic" means that the nanoparticles are substantially free of carbon. As used herein, the term "organic" means that the nanoparticles are composed substantially of carbon. As used herein, the term "colloid" refers to the minute particles suspended in the continuous medium, said particles having a nanometer-scale particle size. As used herein, the term "colloid-forming" refers to substances that form minute particles when dispersed in aqueous solution, i.e., "colloid-forming" polymeric acids are not water-soluble.

[0013] In one embodiment, the new compositions are deposited to form buffer layers in an electronic device. The term "buffer layer" as used herein, is intended to mean an electrically conductive or semiconductive layer which can be used between an anode and an active organic material. A buffer layer is believed to accomplish one or more function in an organic electronic device, including, but not limited to planarization of the underlying layer, hole transport, hole injection, scavenging of impurities, such as oxygen and metal ions, among other aspects to facilitate or to improve the performance of an organic electronic device.

[0014] The term "layer" or "film" refers to a coating covering a desired area. The area can be as large as an entire device or as small as a specific functional area such as the actual visual display area when used in the fabrication of an organic light emitting display, or as small as a single sub-pixel. Films can be formed by any conventional deposition technique, including vapor deposition and liquid deposition. Typical liquid deposition techniques include, but are not limited to, continuous deposition techniques such as spin coating, gravure coating, curtain coating, dip coating, slot-die coating, spray coating, and continuous nozzle coating; and discontinuous deposition techniques such as ink jet printing, gravure printing, and screen printing.

[0015] Other organic electronic devices that may benefit from having one or more layers comprising the new composition include (1) devices that convert electrical energy into radiation (e.g., a light-emitting diode, light-emitting diode display, or diode laser), (2) devices that detect signals through electronics processes (e.g., photodetectors, photoconductive cells, photoresistors, photoswitches, phototransistors, phototubes, IR detectors), (3) devices that convert radiation into electrical energy (e.g., a photovoltaic device or solar cell), and (4) devices that include one or more electronic components that include one or more organic semi-conductor layers, (.e.g., a transistor or diode). Other uses for the new composition include coating materials for memory storage devices, anti-static films, biosensors, electrochromic devices, solid electrolyte capacitors, energy storage devices such as rechargeable batteries, and electromagnetic shielding.

[0016] As used herein, the terms "comprise," "comprising," "include," "including," "has," "having" or any other variation thereof, are intended to cover a non-exclusive inclusion. For example, a process, method, article, or apparatus that comprises a list of elements is not necessarily limited to only those elements but may include other elements not expressly listed or inherent to such process, method, article, or apparatus. Further, unless expressly stated to the contrary, "or" refers to an inclusive or and not to an exclusive or. For example, a condition A or B is satisfied by any one of the following: A is true (or present) and B is false (or not present), A is false (or not present) and B is true (or present), and both A and B are true (or present).

[0017] Also, use of the "a" or "an" are employed to describe elements and components of the invention. This is done merely for convenience and to give a general sense of the invention. This description should be read to include one or at least one and the singular also includes the plural unless it is obvious that it is meant otherwise.

[0018] In one embodiment, buffer layers containing organic nanoparticles have a much lower conductivity than buffer layers without such nanoparticles. In one embodiment, when incorporated into an electroluminescent (EL) device, buffer layers according to the new composition provide high resistance while contributing to improved efficiency and stress life of the EL device.

[0019] In accordance with another embodiment of the new composition, buffer layers comprising the new composition have a pH that is adjusted to a more basic level for improved performance of organic electronic devices.

[0020] In accordance with another embodiment of the new composition, there are provided electroluminescent devices comprising buffer layers deposited from the new composition, which have improved device efficiency and stress-life.

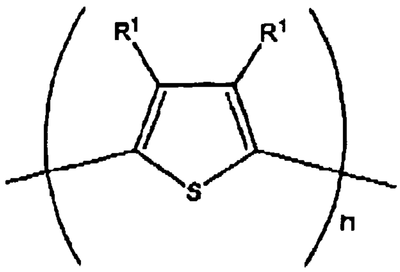
[0021] In accordance with a further embodiment of the new composition, there are provided methods for reducing the conductivity of an electrically conductive organic polymer film deposited from an aqueous dispersion of an electrically conducting polymer onto a substrate, comprising adding a plurality of nanoparticles to the aqueous dispersion.

[0022] In a still further embodiment of the new composition, there are provided methods for producing buffer layers having increased thickness, the method comprising adding a plurality of nanoparticles to an aqueous dispersion of a conductive organic polymer, and depositing a buffer layer from said aqueous dispersion onto a substrate.

[0023] In another embodiment, the new compositions further comprise aqueous electrically conducting polymer dispersions comprising at least one organic nano-particles further comprising at least one dispersing agent.

[0024] The new compositions typically contain a continuous aqueous phase in which at least one of the electrically conducting organic polymers is dispersed. In one embodiment, the electrically conductive organic polymer is selected from polythiophenes as defined in claim 1, polypyrroles as defined in claim 1, and combinations thereof.

[0025] In another embodiment, the electrically conductive organic polymer is a polythiophene ("PTh"). Polythiophenes contemplated for use in the new composition comprise Formula III below:



(III)

wherein:

R^1 is independently selected so as to be the same or different at each occurrence and is selected from hydrogen, alkyl, alkenyl, alkanoyl, alkythio, aryloxy, alkylthioalkyl, alkylaryl, arylalkyl, amino, alkylamino, dialkylamino, aryl, alkylsulfinyl, alkoxyalkyl, alkylsulfonyl, arylthio, arylsulfinyl, alkoxycarbonyl, arylsulfonyl, acrylic acid, phosphoric acid, phosphonic acid, halogen, nitro, cyano, hydroxyl, epoxy, silane, siloxane, alcohol, amidosulfonate, benzyl, carboxylate, ether, ether carboxylate, ether sulfonate, sulfonate, sulfonate, and urethane; or both R^1 groups together may form an alkylene or alkenylene chain completing a 3, 4, 5, 6, or 7-membered aromatic or alicyclic ring, which ring may optionally include one or more divalent nitrogen, sulfur or oxygen atoms, and

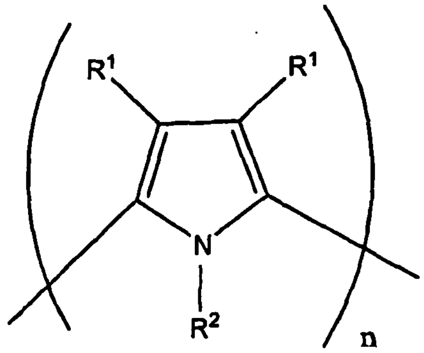
n is at least about 4.

[0026] In one embodiment, both R^1 together form -O-$(CHY)_m$-O-, where m is 2 or 3, and Y is the same or different at each occurrence and is selected from hydrogen, alkyl, alcohol, amidosulfonate, benzyl, carboxylate, ether, ether carboxylate, ether sulfonate, sulfonate, sulfonate, and urethane. In one embodiment, all Y are hydrogen. In one embodiment, the polythiophene is poly(3,4-ethylenedioxythiophene). In one embodiment, at least one Y group is not hydrogen. In one embodiment, at least one Y group is a substituent having F substituted for at least one hydrogen. In one embodiment, at least one Y group is perfluorinated.

[0027] In one embodiment, the polythiophene is a poly[(sulfonic acid-propylene-ether-methylene-3,4-dioxyethylene) thiophene]. In one embodiment, the polythiophene is a poly[(propyl-ether-ethylene-3,4-dioxyethylene)thiophene].

[0028] The polythiophenes of the new composition can be homopolymers, or they can be copolymers of two or more thiophene monomers.

[0029] In another embodiment, the electrically conductive organic polymer is a polypyrole ("PPy"). Polypyrroles contemplated for use the new composition comprise Formula IV below.



(IV)

wherein:

n is at least about 4;

R^1 is independently selected so as to be the same or different at each occurrence and is selected from hydrogen, alkyl, alkenyl, alkoxy, alkanoyl, alkythio, aryloxy, alkylthioalkyl, alkylaryl, arylalkyl, amino, alkylamino, dialkylamino, aryl, alkylsulfinyl, alkoxyalkyl, alkylsulfonyl, arylthio, arylsulfinyl, alkoxycarbonyl, arylsulfonyl, acrylic acid, phosphoric acid, phosphonic acid, halogen, nitro, cyano, hydroxyl, epoxy, silane, siloxane, alcohol, amidosulfonate, benzyl, carboxylate, ether, ether carboxylate, ether sulfonate, sulfonate, sulfonate, and urethane; or both R^1 groups together may form an alkylene or alkenylene chain completing a 3, 4, 5, 6, or 7-membered aromatic or alicyclic ring, which ring may optionally include one or more divalent nitrogen, sulfur or oxygen atoms; and

R^2 is independently selected so as to be the same or different at each occurrence and is selected from hydrogen, alkyl, alkenyl, aryl, alkanoyl, alkylthioalkyl, alkylaryl, arylalkyl, amino, epoxy, silane, siloxane, alcohol, amidosulfonate, benzyl, carboxylate, ether, ether carboxylate, ether sulfonate, sulfonate, and urethane.

[0030] In one embodiment, R^1 is the same or different at each occurrence and is independently selected from hydrogen, alkyl, alkenyl, alkoxy, cycloalkyl, cycloalkenyl, alcohol, amidosulfonate, benzyl, carboxylate, ether, ether carboxylate, ether sulfonate, sulfonate, urethane, epoxy, silane, siloxane, and alkyl substituted with one or more of sulfonic acid, carboxylic acid, acrylic acid, phosphoric acid, phosphonic acid, halogen, nitro, cyano, hydroxyl, epoxy, silane, or siloxane moieties.

[0031] The polypyrroles of the new composition can be homopolymers, or they can be copolymers of two or more pyrrole monomers.

[0032] As used herein, the term "alkyl" refers to a group derived from an aliphatic hydrocarbon and includes linear, branched and cyclic groups which may be unsubstituted or substituted. The term "heteroalkyl" is intended to mean an alkyl group, wherein one or more of the carbon atoms within the alkyl group has been replaced by another atom, such as nitrogen, oxygen, sulfur, and the like. The term "alkylene" refers to an alkyl group having two points of attachment.

[0033] As used herein, the term "alkenyl" refers to a group derived from an aliphatic hydrocarbon having at least one carbon-carbon double bond, and includes linear, branched and cyclic groups which may be unsubstituted or substituted. The term "heteroalkenyl" is intended to mean an alkenyl group, wherein one or more of the carbon atoms within the alkenyl group has been replaced by another atom, such as nitrogen, oxygen, sulfur, and the like. The term "alkenylene" refers to an alkenyl group having two points of attachment.

[0034] As used herein, the following terms for substituent groups refer to the formulae give below:

"alcohol"	$-R^3-OH$
"amidosulfonate"	$-R^3-C(O)N(R^6)R^4-SO_3Z$
"benzyl"	$-CH_2-C_6H_5$
"carboxylate"	$-R^3-C(O)O-Z$
"ether"	$-R^3-O-R^5$
"ether carboxylate"	$-R^3-O-R^4-C(O)O-Z$
"ether sulfonate"	$-R^3-SO_3Z$
"sulfonate"	$-R^3-O-R^4-SO_3Z$
"urethane"	$-R^3-O-C(O)-N(R^6)_2$

where all "R" groups are the same or different at each occurrence and:

R^3 is a single bond or an alkylene group
R^4 is an alkylene group
R^5 is an alkyl group
R^6 is hydrogen or an alkyl group
Z is H, alkali metal, alkaline earth metal, $N(R^5)_4$ or R^5

Any of the above groups may further be unsubstituted or substituted, and any group may have F substituted for one or more hydrogens, including perfluorinated groups.

[0035] In one embodiment, the electrically conductive organic polymers used in the new compositions and methods are typically prepared by oxidatively polymerizing the corresponding monomers in aqueous solution containing a water soluble acid. In one embodiment, the acid is a water-soluble polymeric acid, such as poly(styrenesulfonic acid) ("PSSA"), or poly(2-acrylamido-2-methyl-1-propanesulfonic acid) ("PAAMPSA"), and mixtures thereof. The oxidative polymerization is carried out using an oxidizing agent such as ammonium persulfate, sodium persulfate, and mixtures thereof. Thus, for example, when aniline is oxidatively polymerized in the presence of PAAMPSA, the electrically conductive acid/base salt PAni/PAAMPSA is formed. When ethylenedioxythiophene (EDT) is oxidatively polymerized in the presence of PSSA, the electrically conductive poly(ethylenedioxythiophene) ("PEDT")/PSS is formed. The conjugated backbone of PEDT is partially oxidized and positively charged. Part of the PSSA acts as counter anions to balance the positively charged PEDT backbone. Oxidatively polymerized polypyrrole also has a positive charge which is balanced by the acid anion.

[0036] In one embodiment, the aqueous solution also can include a polymerization catalyst such as ferric sulfate, ferric chloride, and the like, which has a higher oxidizing potential than ammonium persulfate, and the like. The polymerization is typically carried out at low temperatures, e.g., between -10°C and 30°C. After completion of the polymerization reaction, the polymers are optionally isolated by precipitation from aqueous dispersion using a non-solvent for the polymers, e.g., acetone, and the like. When the electrically conductive organic polymer is isolated, the material is typically refined to produce polymer particles having a size less than about 1000 nm. In one embodiment, the polymer particles are less than about 500 nm. In another embodiment, the polymer particles are less than about 50 nm. The isolated electrically conductive organic polymer particles are then either directly combined with an aqueous dispersion of nanoparticles or the conductive organic polymer particles are redispersed in water prior to combination with an aqueous dispersion of nanoparticles.

[0037] In another embidiment, the aqueous electrically conducting polymer dispersion can be combined directly with nanoparticles without predispersing the nanoparticles.

[0038] The new composition may further comprise at least one co-dispersing liquid or at least one co-acid, or a mixture thereof.

[0039] The co-acid can be an inorganic acid, such as HCl, sulfuric acid, or an organic acid, such as acetic acid, p-toluenesulfonic acid. Alternatively, the co-acid can be a water-soluble polymeric acid such as poly(styrenesulfonic acid). Combinations of co-acids can be used.

[0040] The co-acid can be added during the preparation of the new composition at any time of the polymerization or at any time after the polymerization.

[0041] Suitable co-dispersing liquids include ethers, alcohols, alcohol ethers, cyclic ethers, ketones, nitriles, sulfoxides, amides, and combinations thereof. In one embodiment, the co-dispersing liquid comprises at least an alcohol. In one embodiment, the co-dispersing liquid comprises at least one organic solvent selected from n-propanol, isopropanol, t-butanol, dimethylacetamide, dimethyformamide, N-methyl pyrrolidone, and mixtures thereof.

[0042] In one embodiment, the amount of co-dispersing liquid is less than about 60% by volume. In one embodiment, the amount of the co-dispersing liquid is between about 5 and 50% by volume.

[0043] The co-dispersing liquid can be added to the composition at any point in the process of making the new compositions.

[0044] In one embodiment, organic additives, such as steric stabilizers or dispersing agents, may optionally be added to the aqueous solution prior to oxidative polymerization. These additives facilitate formation of electrically conductive organic polymers having nanometer sized particles. Organic additives include, for example, polyacrylamide, polyvinylalcohol, poly(2-vinylpyridine), poly(vinyl acetate), poly(vinyl methyl ether), poly(vinylpyrrolidone), poly(vinyl butyral), and mixtures thereof. Other additives may include dyes, coating aids, conductive inks and pastes, charge transport materials, and mixtures of all of the above and polymeric acids described below.

[0045] The nanoparticles are polymeric acid colloid-particles. Colloid-forming polymeric acids typically have a molecular weight in the range of about 10,000 to about 4,000,000. In one embodiment, the polymeric acids have a molecular weight of about 100,000 to about 2,000,000. Polymeric acid colloid particle size typically ranges from 2 nanometers (nm) to about 140 nm. In one embodiment, the composition comprises polymeric acid colloid particles have a particle size of about 2 nm to about 30 nm.

[0046] The polymeric acid colloids comprise colloids from at lest one acid selected from polymeric sulfonic acids, wherein the at least one polymeric acid is fluorinated. In another embodiment, the new composition comprises at least one perfluorinated polymeric sulfonic acid, polymeric acrylic acids, and mixtures thereof. The polymeric sulfonic acid is fluorinated. In still another embodiment, the colloid-forming polymeric sulfonic acid is perfluorinated. In yet another embodiment, the colloid-forming polymeric sulfonic acid comprises a perfluoroalkylenesulfonic acid.

[0047] In still another embodiment, the colloid-forming polymeric acid comprises a highly-fluorinated sulfonic acid polymer ("FSA polymer"). "Highly fluorinated" means that at least about 50% of the total number of halogen and hydrogen atoms in the polymer are fluorine atoms, an in one embodiment at least about 75%, and in another embodiment at least about 90%. In one embodiment, the polymer is perfluorinated. The term "sulfonate functional group" refers to either to sulfonic acid groups or salts of sulfonic acid groups, and in one embodiment alkali metal or ammonium salts. The functional group is represented by the formula - SO_3X where X is a cation, also known as a "counterion". X may be H, Li, Na, K or $N(R_1)(R_2)(R_3)(R_4)$, and R_1, R_2, R_3, and R_4 are the same or different and are in one embodiment H, CH_3 or C_2H_5. In another embodiment, X is H, in which case the polymer is said to be in the "acid form". X may also be multivalent, as represented by such ions as Ca^{++}, and Al^{+++}. It is clear to the skilled artisan that in the case of multivalent counterions, represented generally as M^{n+}, the number of sulfonate functional groups per counterion will be equal to the valence "n".

[0048] In one embodiment, the FSA polymer comprises a polymer backbone with recurring side chains attached to the backbone, the side chains carrying cation exchange groups. Polymers include homopolymers or copolymers of two or more monomers. Copolymers are typically formed from a nonfunctional monomer and a second monomer carrying the cation exchange group or its precursor, e.g., a sulfonyl fluoride group ($-SO_2F$), which can be subsequently hydrolyzed to a sulfonate functional group. For example, copolymers of a first fluorinated vinyl monomer together with a second fluorinated vinyl monomer having a sulfonyl fluoride group ($-SO_2F$) can be used. Possible first monomers include tetrafluoroethylene (TFE), hexafluoropropylene, vinyl fluoride, vinylidine fluoride, trifluoroethylene, chlorotrifluoroethylene, perfluoro(alkyl vinyl ether), and combinations thereof. TFE is a preferred first monomer.

[0049] In other embodiments, one other monomer includes fluorinated vinyl ethers with sulfonate functional groups or precursor groups which can provide the desired side chain in the polymer. Additional monomers, including ethylene, propylene, and $R-CH=CH_2$ where R is a perfluorinated alkyl group of 1 to 10 carbon atoms, can be incorporated into these polymers if desired. The polymers may be of the type referred to herein as random copolymers, that is copolymers made by polymerization in which the relative concentrations of the co-monomers are kept as constant as possible, so that the distribution of the monomer units along the polymer chain is in accordance with their relative concentrations and relative reactivities. Less random copolymers, made by varying relative concentrations of monomers in the course of the polymerization, may also be used. Polymers of the type called block copolymers, such as that disclosed in European Patent Application No. 1 026 152 A1, may also be used.

[0050] In one embodiment, FSA polymers for use in the new composition include a highly fluorinated, and in one embodiment perfluorinated, carbon backbone and side chains represented by the formula

$$-(O-CF_2CFR_f)_a-O-CF_2CFR'_fSO_3X$$

wherein Rf and R'f are independently selected from F, Cl or a perfluorinated alkyl group having 1 to 10 carbon atoms, a = 0, 1 or 2, and X is H, Li, Na, K or N(R1)(R2)(R3)(R4) and R1, R2, R3, and R4 are the same or different and are and in one embodiment H, CH_3 or C_2H_5. In another embodiment X is H. As stated above, X may also be multivalent.

[0051] In one embodiment, the FSA polymers include, for example, polymers disclosed in U.S. Patent No. 3,282,875 and in U.S. Patent Nos. 4,358,545 and 4,940,525. An example of preferred FSA polymer comprises a perfluorocarbon backbone and the side chain represented by the formula

$$-O-CF_2CF(CF_3)-O-CF_2CF_2SO_3X$$

where X is as defined above. FSA polymers of this type are disclosed in U.S. Patent No. 3,282,875 and can be made by copolymerization of tetrafluoroethylene (TFE) and the perfluorinated vinyl ether $CF_2=CF-O-CF_2CF(CF_3)-O-CF_2CF_2SO_2F$, perfluoro(3,6-dioxa-4-methyl-7-octenesulfonyl fluoride) (PDMOF), followed by conversion to sulfonate groups by hydrolysis of the sulfonyl fluoride groups and ion exchanged as necessary to convert them to the desired ionic form. An example of a polymer of the type disclosed in U.S. Patent Nos. 4,358,545 and 4,940,525 has the side chain $-O-CF_2CF_2SO_3X$, wherein X is as defined above. This polymer can be made by copolymerization of tetrafluoroethylene (TFE) and the perfluorinated vinyl ether $CF_2=CF-O-CF_2CF_2SO_2F$, perfluoro(3-oxa-4-pentenesulfonyl fluoride) (POPF), followed by hydrolysis and further ion exchange as necessary.

[0052] In one embodiment, the FSA polymers for use in this new composition typically have an ion exchange ratio of less than about 33. In this application, "ion exchange ratio" or "IXR" is defined as number of carbon atoms in the polymer backbone in relation to the cation exchange groups. Within the range of less than about 33, IXR can be varied as desired for the particular application. In one embodiment, the IXR is about 3 to about 33, and in another embodiment about 8 to about 23.

[0053] The cation exchange capacity of a polymer is often expressed in terms of equivalent weight (EW). For the purposes of this application, equivalent weight (EW) is defined to be the weight of the polymer in acid form required to neutralize one equivalent of sodium hydroxide. In the case of a sulfonate polymer where the polymer has a perfluorocarbon backbone and the side chain is $-O-CF_2-CF(CF_3)-O-CF_2-CF_2-SO_3H$ (or a salt thereof), the equivalent weight range which corresponds to an IXR of about 8 to about 23 is about 750 EW to about 1500 EW. IXR for this polymer can be related to equivalent weight using the formula: 50 IXR + 344 = EW. While the same IXR range is used for sulfonate polymers disclosed in U.S. Patent Nos. 4,358,545 and 4,940,525, e.g., the polymer having the side chain $-O-CF_2CF_2SO_3H$ (or a salt thereof), the equivalent weight is somewhat lower because of the lower molecular weight of the monomer unit containing a cation exchange group. For the preferred IXR range of about 8 to about 23, the corresponding equivalent weight range is about 575 EW to about 1325 EW. IXR for this polymer can be related to equivalent weight using the formula: 50 IXR + 178 = EW.

[0054] The FSA polymers can be prepared as colloidal aqueous dispersions. They may also be in the form of dispersions in other media, examples of which include, but are not limited to, alcohol, water-soluble ethers, such as tetrahydrofuran, mixtures of water-soluble ethers, and combinations thereof. In making the dispersions, the polymer can be used in acid form. U.S. Patent Nos. 4,433,082, 6,150,426 and WO 03/006537 disclose methods for making of aqueous alcoholic dispersions. After the dispersion is made, concentration and the dispersing liquid composition can be adjusted by methods known in the art.

[0055] In one embodiment, aqueous dispersions of the colloid-forming polymeric acids, including FSA polymers, have particle sizes as small as possible and an EW as small as possible, so long as a stable colloid is formed.

[0056] Aqueous dispersions of FSA polymer are available commercially as Nafion® dispersions, from E. I. du Pont de Nemours and Company (Wilmington, DE).

[0057] In one embodiment, the aqueous electrically conductive polymer dispersions are combined with an aqueous dispersion of colloid-forming polymeric acid and further blended using sonication or microfluidization to ensure mixing of the components.

[0058] Dispersions of electrically conductive polymers generally have a fairly low pH due to the presence of acids in the oxidative polymerization process. For example, aqueous poly(ethylenedioxythiophene) ("PEDT") dispersions, available commercially as Baytron®-P VP Al 4083 and CH8000, from H. C. Starck, GmbH, Leverkusen, Germany, have a pH below 2. It is frequently desirable to have aqueous dispersions of conductive polymers with a higher pH, as the acidity can be corrosive. With Baytron-P, adjusting the pH to higher levels canhave a deleterious effect on the electrical properties of the conductive polymer and the functional effectiveness as a buffer layer in OLEDs. In new compositions comprising aqueous dispersions of at least one electrically conducting polymer and nanoparticles of colloid-forming polymeric acids, it has been found that the pH can be adjusted without sacrificing electrical properties. The pH can be adujusted using known techniques, for example, ion exchange or by titration with an aqueous basic solution. Stable dispersions of conductive polymers and colloid-forming polymeric acids can be formed with a pH adjusted from 1 to 8. Adjusting the pH to higher, more neutral values, does not deleteriously affect the electrical properties and device performance of the conductive polymers in the new composition, and in most cases improves those properties.

[0059] In one embodiment, the mixture of the electrically conductive polymer and colloid-forming polymeric acid is contacted with at least one ion exchange resin under conditions suitable to produce a stable, aqueous dispersion. In one embodiment, the mixture of the electrically conductive polymer and colloid-forming polymeric acid is contacted with a first ion exchange resin and a second ion exchange resin.

[0060] In another embodiment, the first ion exchange resin is an acidic, cation exchange resin, such as a sulfonic acid cation exchange resin set forth above, and the second ion exchange resin is a basic, anion exchange resin, such as a tertiary amine or a quaternary exchange resin.

[0061] Ion exchange is a reversible chemical reaction wherein an ion in a fluid medium (such as an aqueous dispersion) is exchanged for a similarly charged ion attached to an immobile solid particle that is insoluble in the fluid medium. The term "ion exchange resin" is used herein to refer to all such substances. The resin is rendered insoluble due to the crosslinked nature of the polymeric support to which the ion exchanging groups are attached. Ion exchange resins are classified as acidic, cation exchangers, which have positively charged mobile ions available for exchange, and basic, anion exchangers, whose exchangeable ions are negatively charged.

[0062] Both acidic, cation exchange resins and basic, anion exchange resins are contemplated for use in the new composition. In one embodiment, the acidic, cation exchange resin is an organic acid, cation exchange resin, such as a sulfonic acid cation exchange resin. Sulfonic acid cation exchange resins contemplated for use in the new composition include, for example, sulfonated styrene-divinylbenzene copolymers, sulfonated crosslinked styrene polymers, phenol-formaldehyde-sulfonic acid resins, benzene-formaldehyde-sulfonic acid resins, and mixtures thereof. In another embodiment, the acidic, cation exchange resin is an organic acid, cation exchange resin, such as carboxylic acid, acrylic or phosphoric acid cation exchange resin. In addition, mixtures of different cation exchange resins can be used. In many cases, the basic ion exchange resin can be used to adjust the pH to the desired level. In some cases, the pH can be further increased with an aqueous basic solution such as a solution of sodium hydroxide, ammonium hydroxide, tetramethylammonium hydroxide, or the like. In other cases the pH can be further reduced with acidic ion-exchange resins for the applications where high acidicity is not an issue.

[0063] In another embodiment, the basic, anionic exchange resin is a tertiary amine anion exchange resin. Tertiary amine anion exchange resins contemplated for use in the new composition include, for example, tertiary-aminated styrene-divinylbenzene copolymers, tertiary-aminated crosslinked styrene polymers, tertiary-aminated phenol-formaldehyde resins, tertiary-aminated benzene-formaldehyde resins, and mixtures thereof. In a further embodiment, the basic, anionic exchange resin is a quaternary amine anion exchange resin, or mixtures of these and other exchange resins.

[0064] The first and second ion exchange resins may contact the mixture of the electrically conductive polymer and colloid-forming polymeric acid either simultaneously, or consecutively. For example, in one embodiment both resins are added simultaneously to a mixture of the electrically conductive polymer and colloid-forming polymeric acid, and allowed to remain in contact with the dispersion for at least about 1 hour, e.g., about 2 hours to about 20 hours. The ion exchange resins can then be removed from the dispersion by filtration. The size of the filter is chosen so that the relatively large ion exchange resin particles will be removed while the smaller dispersion particles will pass through. The basic, anion exchange and/or acidic, cation exchange resins the acidic sites more basic, resulting in increased pH of the dispersion. In general, at least 1 gram of ion exchange is used per about 1 gram of solids in the mixture of the electrically conductive polymer and colloid-forming polymeric acid. In other embodiments, the use of the ion exchange resin is used in a ratio of up to about 5 grams of ion exchange resin to solids in the mixture of the electrically conductive polymer and colloid-forming polymeric acid, and depends on the pH that is to be achieved. In one embodiment, about one gram of Lewatit® MP62 WS, a weakly basic anion exchange resin from Bayer GmbH, and about one gram of Lewatit® MonoPlus S100, a strongly acidic, sodium cation exchange resin from Bayer, GmbH, are used per gram of solids in the mixture of the electrically conductive polymer and colloid-forming polymeric acid.

[0065] Nanoparticles contemplated for use in the new composition may have a variety of shapes and sizes and mixtures of shapes and sizes. In one embodiment, the nanoparticles are substantially spherical. Nanoparticles contemplated for use in the new composition typically have an average particle diameter less than about 500 nm. In another embodiment, the nanoparticles have an average particle diameter less than about 100 nm. In still another embodiment, the nanoparticles have an average particle diameter less than about 50 nm.

[0066] Aspect ratio is defined as ratio of particle width to particle length. For elongated particles, the "particle size" is considered to be the particle width. In another embodiment, the nano-particles have an irregular geometry. For irregularly-shaped particles, the "particle size" is considered to be size of the smallest screen opening through which the particle will pass.

[0067] In another embodiment, there are provided buffer layers deposited from aqueous dispersions comprising electrically conductive polymers and inorganic nanoparticles. Both the electrically conducting polymers and the nanoparticles can be readily dispersed in water. In one embodiment, continuous, smooth films can be produced by depositing from aqueous dispersions containing electrically conducting polymers and nanoparticles.

[0068] In one embodiment, buffer layers comprising the new composition have a reduced conductivity relative to buffer layers of identical composition except the inorganic nanoparticles are absent. Electrical resistivity is inversely proportional to electrical conductivity. Thus, as employed herein, the phrases "high resistance" and "low conductivity" are used interchangeably with reference to the buffer layers described herein. As used herein, the phrases "high resistance" and "low conductivity" each refer to a conductivity level less than that of a commercially available buffer layers, i.e., less than about 1.0×10^{-3} S/cm. In another embodiment, the resistivities preferably less than 1.0×10^{-5} S/cm. Resistivity and conductivity values are typically reported in units of ohm-centimeter (ohm-cm) and Siemens per centimeter (S/cm), respectively. As used herein, conductivity values are reported (using the unit S/cm) rather than resistivity values.

[0069] In one embodiment, the organic electronic device comprises an electroactive layer positioned between two electrical contact layers, wherein at least one of the layers of the device includes the new buffer layer. One embodiment is Illustrated in one type of OLED device, as shown in FIG. 1, which is a device that has anode layer 110, a buffer layer 120, an electroluminescent layer 130, and a cathode layer 150. Adjacent to the cathode layer 150 is an optional electron-injection/transport layer 140. Between the buffer layer 120 and the cathode layer 150 (or optional electron injection/transport layer 140) is the electroluminescent layer 130.

[0070] The device may include a support or substrate (not shown) that can be adjacent to the anode layer 110 or the cathode layer 150. Most frequently, the support is adjacent the anode layer 110. The support can be flexible or rigid, organic or inorganic. Generally, glass or flexible organic films are used as a support. The anode layer 110 is an electrode that is more efficient for injecting holes than the cathode layer 150. The anode can include materials containing a metal, mixed metal, alloy, metal oxide or mixed oxide. Suitable materials include the mixed oxides of the Group 2 elements (i.e., Be, Mg, Ca, Sr, Ba, Ra), the Group 11 elements, the elements in Groups 4, 5, and 6, and the Group 8-10 transition elements. If the anode layer 110 is to be light transmitting, mixed oxides of Groups 12, 13 and 14 elements, such as indium-tin-oxide, may be used. As used herein, the phrase "mixed oxide" refers to oxides having two or more different cations selected from the Group 2 elements or the Groups 12, 13, or 14 elements. Some non-limiting, specific examples of materials for anode layer 110 include indium-tin-oxide ("ITO"), aluminum-tin-oxide, gold, silver, copper, and nickel. The anode may also comprise an organic material such as polyaniline or polythiophene.

[0071] The anode layer 110 may be formed by a chemical or physical vapor deposition process or spin-deposit process. Chemical vapor deposition may be performed as a plasma-enhanced chemical vapor deposition ("PECVD") or metal organic chemical vapor deposition ("MOCVD"). Physical vapor deposition can include all forms of sputtering, including ion beam sputtering, as well as e-beam evaporation and resistance evaporation. Specific forms of physical vapor deposition include rf magnetron sputtering and inductively-coupled plasma physical vapor deposition ("IMP-PVD"). These deposition techniques are well known within the semiconductor fabrication arts.

[0072] Usually, the anode layer 110 is patterned during a lithographic operation. The pattern may vary as desired. The layers can be formed in a pattern by, for example, positioning a patterned mask or resist on the first flexible composite barrier structure prior to applying the first electrical contact layer material. Alternatively, the layers can be applied as an overall layer (also called blanket deposit) and subsequently patterned using, for example, a patterned resist layer and wet chemical or dry etching techniques. Other processes for patterning that are well known in the art can also be used. When the electronic devices are located within an array, the anode layer 110 typically is formed into substantially parallel strips having lengths that extend in substantially the same direction.

[0073] The buffer layer 120 can be deposited onto substrates using any technique well-known to those skilled in the art.

[0074] The electroluminescent (EL) layer 130 may typically be any organic EL material, including, but not limited to, fluorescent dyes, fluorescent and phosphorescent metal complexes, conjugated polymers, and mixtures thereof. Examples of fluorescent dyes include, but are not limited to, pyrene, perylene, rubrene, derivatives thereof, and mixtures thereof. Examples of metal complexes include, but are not limited to, metal chelated oxinoid compounds, such as tris (8-hydroxyquinolato)aluminum (Alq3); cyclometalated iridium and platinum electroluminescent compounds, such as complexes of Iridium with phenylpyridine, phenylquinoline, or phenylpyrimidine ligands as disclosed in Petrov et al., Published PCT Application WO 02/02714, and organometallic complexes described in, for example, published applications US 2001/0019782, EP 1191612, WO 02/15645, and EP 1191614; and mixtures thereof. Electroluminescent emissive layers comprising a charge carrying host material and a metal complex have been described by Thompson et al., in U.S. Patent 6,303,238, and by Burrows and Thompson in published PCT applications WO 00/70655 and WO 01/41512. Examples of conjugated polymers include, but are not limited to poly(phenylenevinylenes), polyfluorenes, poly(spirobifluorenes), polythiophenes, poly(p-phenylenes), copolymers thereof, and mixtures thereof.

[0075] The particular material chosen may depend on the specific application, potentials used during operation, or other factors. The EL layer 130 containing the electroluminescent organic material can be applied using any number of techniques including vapor deposition, solution processing techniques or thermal transfer. In another embodiment, an EL polymer precursor can be applied and then converted to the polymer, typically by heat or other source of external energy (e.g., visible light or UV radiation).

[0076] Optional layer 140 can function both to facilitate electron injection/transport, and also serve as a confinement layer to prevent quenching reactions at layer interfaces. More specifically, layer 140 may promote electron mobility and reduce the likelihood of a quenching reaction if layers 130 and 150 would otherwise be in direct contact. Examples of materials for optional layer 140 include metal-chelated oxinoid compounds (e.g., Alq_3 or the like); phenanthroline-based compounds (e.g., 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline ("DDPA"), 4,7-diphenyl-1,10-phenanthroline ("DPA"), or the like); azole compounds (e.g., 2-(4-biphenylyl)-5-(4-t-butylphenyl)-1,3,4-oxadiazole ("PBD" or the like), 3-(4-biphenylyl)-4-phenyl-5-(4-t-butylphenyl)-1,2,4-triazole ("TAZ" or the like); other similar compounds; or any one or more combinations thereof. Alternatively, optional layer 140 may be inorganic and comprise BaO, LiF, Li_2O, or the like.

[0077] The cathode layer 150 is an electrode that is particularly efficient for injecting electrons or negative charge carriers. The cathode layer 150 can be any metal or nonmetal having a lower work function than the first electrical contact layer (in this case, the anode layer 110). As used herein, the term "lower work function" is intended to mean a material having a work function no greater than about 4.4 eV. As used herein, "higher work function" is intended to mean a material having a work function of at least approximately 4.4 eV.

[0078] Materials for the cathode layer can be selected from alkali metals of Group 1 (e.g., Li, Na, K, Rb, Cs,), the Group 2 metals (e.g., Mg, Ca, Ba, or the like), the Group 12 metals, the lanthanides (e.g., Ce, Sm, Eu, or the like), and the actinides (e.g., Th, U, or the like). Materials such as aluminum, indium, yttrium, and combinations thereof, may also be used. Specific non-limiting examples of materials for the cathode layer 150 include barium, lithium, cerium, cesium, europium, rubidium, yttrium, magnesium, and samarium.

[0079] The cathode layer 150 is usually formed by a chemical or physical vapor deposition process. In general, the cathode layer will be patterned, as discussed above in reference to the anode layer 110. If the device lies within an array, the cathode layer 150 may be patterned into substantially parallel strips, where the lengths of the cathode layer strips extend in substantially the same direction and substantially perpendicular to the lengths of the anode layer strips. Electronic elements called pixels are formed at the cross points (where an anode layer strip intersects a cathode layer strip when the array is seen from a plan or top view).

[0080] In other embodiments, additional layer(s) may be present within organic electronic devices. For example, a layer (not shown) between the buffer layer 120 and the EL layer 130 may facilitate positive charge transport, band-gap matching of the layers, function as a protective layer, or the like. Similarly, additional layers (not shown) between the

EL layer 130 and the cathode layer 150 may facilitate negative charge transport, band-gap matching between the layers, function as a protective layer, or the like. Layers that are known in the art can be used. In addition, any of the above-described layers can be made of two or more layers. Alternatively, some or all of inorganic anode layer 110, the buffer layer 120, the EL layer 130, and cathode layer 150, may be surface treated to increase charge carrier transport efficiency. The choice of materials for each of the component layers may be determined by balancing the goals of providing a device with high device efficiency with the cost of manufacturing, manufacturing complexities, or potentially other factors.

[0081] Depending upon the intended application of the electronic device, the EL layer 130 can be a light-emitting layer that is activated by signal (such as in a light-emitting diode) or a layer of material that responds to radiant energy and generates a signal, with or without an applied potential (such as detectors or voltaic cells). Examples of electronic devices that may respond to radiant energy are selected from photoconductive cells, photoresistors, photoswitches, phototransistors, and phototubes, and photovoltaic cells. After reading this specification, skilled artisans will be capable of selecting material(s) that are suitable for their particular applications. The light-emitting materials may be dispersed in a matrix of another material, with or without additives, but preferably form a layer alone. The EL layer 130 generally has a thickness in the range of approximately 50-500 nm.

[0082] In organic light emitting diodes (OLEDs), electrons and holes, injected from the cathode 150 and anode 110 layers, respectively, into the EL layer 130, form negative and positively charged polarons in the polymer. These polarons migrate under the influence of the applied electric field, forming a polaron exciton with an oppositely charged species and subsequently undergoing radiative recombination. A sufficient potential difference between the anode and cathode, usually less than approximately 12 volts, and in many instances no greater than approximately 5 volts, may be applied to the device. The actual potential difference may depend on the use of the device in a larger electronic component. In many embodiments, the anode layer 110 is biased to a positive voltage and the cathode layer 150 is at substantially ground potential or zero volts during the operation of the electronic device. A battery or other power source(s) may be electrically connected to the electronic device as part of a circuit but is not illustrated in FIG. 1.

[0083] In accordance with another embodiment, there are provided methods for reducing conductivity of an electrically conductive organic polymer film deposit from aqueous dispersion onto a substrate to a value less than about 1 x 10^{-5} S/cm. Such a method can be performed, for example, by adding a plurality of nanoparticles to the aqueous dispersion of electrically conducting polymers. Surprisingly, it has been discovered that even electrically semi-conductive inorganic nanoparticles, when incorporated into an electrically conductive organic polymer film as described herein, reduce the conductivity of the polymer film. In one embodiment, the electrically conductive organic polymer film can be used as a buffer layer in electroluminescent devices. In another embodiment, the electrically conductive polymer film is PPy/PSSA, PEDT/PSSA, and the like.

[0084] In a still further embodiment, there are provided methods for producing buffer layers having increased thickness. Such a method can be performed, for example, by adding a plurality of nanoparticles to an aqueous dispersion of an electrically conductive organic polymer, and depositing a buffer layer from said aqueous dispersion onto a substrate. Addition of nanoparticles to aqueous dispersions of conductive polymers produces aqueous dispersions having an increased viscosity. This enhanced viscosity provides increased control of the thickness of layers deposit from the aqueous solutions. Control of buffer layer thickness is desirable since the appropriate thickness of a properly functioning buffer layer depends to some extent on the surface roughness of the metallic conductive layer onto which the buffer layer is deposited.

[0085] The invention will now be described in greater detail by reference to the following non-limiting examples.

Example 8 (REFERENCE)

[0086] This example illustrates the blending of Nafion® with Baytron-P®, AI4083, by sonication, and ion exchange resin treatment for achieving high pH.

[0087] In this example, a special grade of Baytron-P® AI4083 (LVW 186; solid:2.6%; pH=1.67) was used to form a blend with Nafion®. AI4083 is PEDOT/PSSA from H. C. Starck, GmbH, Leverkusen, Germany. The w/w ratio between PEDOT/PSSA is 1:6. The Nafion® used for the blending is a 26.5% (w/w) aqueous colloidal perfluoroethylenesulfonic acid dispersion with an EW of 1050 and was made using a procedure similar to the procedure in US Patent 6,150,426, Example 1, Part 2, except that the temperature was approximately 270C.

[0088] 9.74 g of the Nafion® was first mixed with 183.99g deionized water. The diluted Nafion® was then dripped in and mixed with 96.84g Baytron-P® in a 500 mL round bottom flask while being stirred with a magnetic stirrer. It took about two and one half hour to complete the addition. Resulting dispersion contains 2.57% solid in which the equivalent ratio between Nafion® /PEDT/PSSA was 2.0/1.0/4.6. The "equivalent ratio" as used herein, is intended to mean the ratio of the number of acid equivalents of the colloid-forming polymeric acid to the number of monomer units of conductive polymer and/or polymeric acid anion. The entire dispersion was then subjected to sonication using an Ultrasonic Processor XL (Heat Systems, Inc., Farmingdale, NY, USA) set at power 7 for total 30 seconds "On" time (15 seconds On/ 15 seconds Off). The dispersion was then checked for particle size using an AccuSizer Model 780A (Particle Sizing Systems, Santa Barbara, CA). Particle size count ("PSC") was 281,329 particles in one mL of dispersion with particles greater than 0.75 μm. Prior to sonication, PSC was 331,329. The dispersion was further subjected to an additional 30 seconds of sonication. The PSC was 75,901. However, an additional 30 seconds didn't show any lowering of PSC.

[0089] The entire amount of dispersion was divided into a one-third portion and a two-thirds portion. The as-made one-third portion ("Sample 8a"), without adjustment of pH, had a pH of 1.8 and conductivity of $6x10^{-5}$S/cm, which was much lower than the conductivity of the starting material AI4083 (~10^{-3}S/cm).

[0090] The two-thirds portion was run through a 100 mL column packed with 9g of Monoplus S100 on the bottom and 9g of MP 62 WS on the top. Monoplus S100 is a trade name from Bayer GmbH, (Pittsburgh, PA) for sodium sulfonate of crosslinked polystyrene, cation exchange resin. MP62 WS is a trade from Bayer for free base/chloride of tertiary/quaternary amine of crosslinked polystyrene, anion exchange resin. The two resins were washed first before use with deionized water separately until there was no color in the water. One half of the resin-treated dispersion was kept as-is ("Sample 8b"). The pH of Sample 8b was 3.8, and the conductivity was $2.0x10^{-4}$S/cm. The other half of the resin-treated dispersion ("Sample 8c") was further treated with sodium hydroxide to raise the pH to 6.5. It had a conductivity of $1.8x10^{-4}$S/cm.

[0091] The three samples of Baytron-P®/Nafion® blends and Baytron-P® were then tested for device performance. Each was spun on glass/ITO substrates (30mmx30mm) having ITO thickness of 100 to 150nm and 15mm x 20mm ITO area for light emission backlight substrates and baked at 200°C in air for 3 minutes. Thickness of the buffer layer is given in Table 3 below. For the light-emitting layer, a 1% (w/v) toluene solution of Lumination Green from Dow Chemicals (Midland, MI) was spin-coated on top of the buffer layer films to a thicknes of 775 Å, and subsequently baked at 100°C in vacuum for 30 minutes. Immediately after, a 3 nm thick barium layer and a 350-400 nm aluminum layer were deposited on the Lumination Green films to serve as a cathode. The device data summarized in Table 3 clearly shows that devices made with Baytron-P®/Nafion® blends have much better device performance than devices made with Baytron-P® alone. In addition, devices made with the high pH (3.8 and 6.5) Baytron-P®/Nafion® blends have higher device efficiency and much higher device lifetime. The lifetime is defined as the time, in hours, for the luminance to drop to one-half the initial level.

Table 3.

Device Performance at 900cd/m^2 and 80°C.				
Buffer	Sample 8a pH=1.8	Sample 8b pH=3.8	Sample 8c pH=6.5	4083
LifeTime (h)	~280	~550	~550	~3
Efficiency (cd/A)	16.0	19.5	18.2	8.0
Voltage (V)	3.3	3.6	3.72	4.1
Buffer Thickness (A)	613	753	764	800

<u>Example 9</u> (REFERENCE)

[0092] This example illustrates the blending of Nafion® with Baytron-P® AI4083 by microfluidization, and ion exchange resin treatment for achieving high pH.

[0093] In this example, Baytron-P® AI4083 (Lot# CHDSPS0006; solid:1.48%, pH=1.77) was used to form a blend with Nafion®. AI4083 is PEDOT/PSSA from H. C. Starck, GmbH, Leverkusen, Germany. The w/w ratio between PEDOT/PSSA is 1:6. The Nafion® used for the blending is a 12.3% (w/w) aqueous colloidal dispersion with an EW of 1050. A 25% (w/w) Nafion® was made first using a procedure similar to the procedure in US Patent 6,150,426, Example 1, Part 2, except that the temperature was approximately 270°C. The Nafion® dispersion was diluted with water to form a 12.3 % (w/w) dispersion for the use of this invention.

[0094] 141.39g of the Nafion® was dripped in to mix with 558.28g Baytron-P® in a 1000 mL flask while being stirred with a magnetic stirrer. It took more than 6 hours to complete the addition. The resulting dispersion contained 3.67% solid in which the equivalent ratio of Nafion®/PEDT/PSSA was 2.0/1.0/4.6.

[0095] A small portion of the dispersion without further processing was retained for taking atom force microscopy (AFM). It had a pH of 1.6 and a film (baked at 90°C for 40 minutes) conductivity of $1.0x10^{-4}$S/cm. AFM showed that the film consisted of a large quantity of broad bumps (50 to 60 nm tall). In many applications this morphology may not be desirable.

[0096] The rest of the dispersion was further processed with a Microfluidizer Processor M-110EH (Microfluidics, Massachusetts, USA) using a pressure of 8,000 psi ("Sample 9a"). The diameters of first chamber and second chamber were 200μm (H30Z model), and 87μm (G10Z), respectively. In one pass, the PSC was reduced from 693,000 to ~240,000. It had a pH of 1.7 and a film (baked at 90°C for 40 minutes) conductivity was measured to be $9.8x10^{-6}$S/cm. AFM shows that the film is much smoother than the as-blended films.

[0097] 100 mL of the microfluidized dispersion was ran through a 100 mL column packed with 9g of Monoplus S100 on the bottom and 9g of MP 62 WS on the top ("Sample 9b"). The two resins were washed first before use with deionized water separately until there was no color in the water. The pH of the resin-treated dispersion is 3.7 and has film (baked at 90°C for 40 minutes) conductivity of $2.3x10^{-5}$S/cm.

[0098] The two samples of Baytron-P®/Nafion® blends and Baytron-P® were then tested for device performance. Each was spun on glass/ITO backlight substrates (30mmx30mm) and baked at 200°C in air for 3 minutes. The substrate had an ITO thickness of 100 to 150nm and an ITO area of 15mm x 20mm ITO for light emission. The thickness of the buffer layer is given in Table 4 below. For the light-emitting layer, a 1 % (w/v) toluene solution of Lumination Green from Dow Chemicals (Midland, Michigan) was spin-coated on top of the buffer layer films and subsequently baked at 100°C in vacuum for 30 minutes. The final thickness was 740 Å . Immediately after, a 3nm thick barium layer and a 350-400nm aluminum layer were deposited on the Lumination Green films to serve as a cathode. The device data clearly shows that devices made with Baytron-P®/Nafion® blends have much better device properties than those made with Baytron-P alone. In addition, the device made with the 3.7 pH Baytron-P/Nafion® blend has much better device lifetime.

Table 4.

Device Performance at 900cd/m² and 80°C.			
Buffer	4083	Sample 9a (pH=1.7)	Sample 9b (pH=3.7)
Lifetime (h)	16	40	220
Efficiency (cd/A)	7.7	13.8	15.0
Voltage (V)	4.19	3.98	4.20
Buffer Thickness (A)	790	846	741

Comparative Example 9

[0099] This compaartive example demonstrates the effect of pH on device performance of Baytron-P® AI4083 (Lot# CHDSPS0006; solid: 1.48%, pH=1.8) without the inclusion of a colloid-forming polymeric acid such as Nafion®.

[0100] 80g AI4083 was added with 4g each of Lewatit S100 and MP 62 WS for 20 minutes. The resins were removed by filtration through VWR #417 filter paper (40μm). The pH was measured to be 2.2 and was adjusted to 3.95 by the addition of 1.0M NaOH aqueous solution. Half of the sample is designated as comp. 9a (see Table 5). The other half was further adjusted with the 1.0M NaOH solution to pH of 7. This sample is designated as comp. 9b.

[0101] Comp. 9a and 9b and AI4083 were then tested for device performance. Each was spun on glass/ITO backlight substrates (30mmx30mm) and baked at 200°C in air for 3 minutes. The substrate had an ITO thickness of 100 to 150nm and an ITO area of 15mm x 20mm for light emission. The thickness of the buffer layer is given in Table 5 below. For the light-emitting layer, a 1 % (w/v) toluene solution of Lumination Green from Dow Chemicals (Midland, Michigan) was spin-coated on top of the buffer layer films and subsequently baked at 100°C in vacuum for 30 minutes. The final thickness was 740 Å. Immediately after, a 3nm thick barium layer and a 300-500nm aluminum layer were deposited on the Lumination Green films to serve as a cathode. The device data summarized in Table 5 clearly shows that Baytron-P® AI4083 has a much higher voltage and much lower efficiency when the pH is increased from 1.8 to 4 or 7. This result clearly shows that Baytron-P® starts to lose effectiveness as a buffer layer when adjusted to a pH greater than ~2.

Table 5

Device Performance at 1,000cd/m² and 25°C.			
Buffer	4083 (pH:1.8)	Comp. 9a (pH=4)	Comp. 9b (pH=7)
Efficiency (cd/A)	3.8	0.2	0.1
Voltage (V)	3.7	4.5	4.6
Buffer Thickness (Å)	815	932	855

Example 10 (REFERENCE)

[0102] This example illustrates the formation of blends of Nafion® and Baytro-P® at different concentrations and pH, and the effect on device performance.

[0103] The Baytron-P® AI4083 (Lot# CHDSPS0006; solid:1.48%, pH=1.8) used in this example is from the same lot as in Example 9 and Comparative Example 9 to form a blend with Nafion®. The Nafion® used for the blending is DE1021, commercially available from E. I. du Pont de Nemours and Company (Wilmington, DE). It is 11.1% (w/w) aqueous colloidal dispersion with an EW of 1050.

[0104] 1.32g of the Nafion® was pipetted by hand in to mix with 98.68g Baytron-P in a 250 mL flask while being stirred with a magnetic stirrer. It was left stirred for 15 minutes. The resulting dispersion contained 1.6% solid in which the equivalent ratio and weight ratio of Nafion®/PEDT/PSSA were 0.1/1.0/4.6 and 0.15/0.21/1.25, respectively.

[0105] The entire dispersion was transferred to a 125 mL plastic bottle with stir bar and then subjected to sonication using an Ultrasonic Processor XL (Heat Systems, Inc., Farmingdale, NY, USA) set at power 7 for total 30 seconds "On" time (15 seconds On/15 seconds Off). The dispersion was then checked for particle size using an AccuSizer Model 780A (Particle Sizing Systems, Santa Barbara, CA). PSC was 419,141 particles in one mL of dispersion with particles greater than 0.75 μm. Prior to sonication, PSC was 423,543.

[0106] The entire amount of dispersion was divided into two equal portions. The as-made one half portion ("Sample 10a"), without adjustment, had a pH of 1.74 and conductivity of 8.6×10^{-4}S/cm, which was much lower than the conductivity of the starting material AI4083 (~10^{-3}S/cm).

[0107] The other half portion was run through a 100 mL column packed with 7.5g of Monoplus S100 on the bottom and 7.5g of MP 62 WS on the top. Monoplus S100 is a trade name from Bayer GmbH (Pittsburgh, PA) for sodium sulfonate of crosslinked polystyrene, cation exchange resin. MP62 WS is a trade from Bayer for free base/chloride of tertiary/quaternary amine of crosslinked polystyrene, anion exchange resin. The two resins were washed first before use with deionized water separately until there was no color in the water. The resin-treated dispersion was designated as Sample 10b. It had a pH of 3.8 and conductivity of was 7.3×10^{-4}S/cm.

[0108] The two samples of Baytron-P®/Nafion® blends with pH of 1.7 and 3.8 were then tested for device performance. Each was spun on glass/ITO backlight substrates (30mmx30mm) and baked at 200°C in air for 3 minutes. The substrate had an ITO thickness of 100 to 150nm and an ITO area of 15mm x 20mm for light emission. The thickness of the buffer layer is given in Table 6 below. For the light-emitting layer, a 1% (w/v) toluene solution of Lumination Green from Dow Chemicals (Midland, Michigan) was spin-coated on top of the buffer layer films and subsequently baked at 100°C in vacuum for 30 minutes. The final thickness was 740 Å. Immediately after, a 3nm thick barium layer and a 350-400nm aluminum layer were deposited on the Lumination Green films to serve as a cathode. The device data clearly shows that for devices made with Baytron-P®/Nafion® blends having a low equivalent ratio of Nafion® to Baytron-P®, the blend with the higher pH has a much lower device efficiency and higher voltage. This trend is opposite from the trend in Example 9, where blends with a higher equivalent ratio of Nafion® to Baytron-P® resulted in devices with a better lifetime and efficiency as pH is increased.

Table 6

Device Performance at 1,000cd/m^2 and 25°C.		
Buffer	Sample 10a (pH=1.7)	Sample 10b (pH=3.8)
Efficiency (cd/A)	9.4	0.9
Voltage (V)	3.94	4.4
Buffer Thickness (A)	835	858

Example 12 (REFERENCE)

[0109] This example illustrates the blending of Nafion® with Baytron-P® CH8000 by sonication, and ion exchange resin treatment for achieving high pH and improved device performance.

[0110] In this example, Baytron-P® CH8000 (Lot# BPSS0007, solid:2.8%; pH~1.7) was used to form a blend with Nafron®. The Nafion® used for the polymerization is DE1021, a commercial grade of Nafion®. It is 11.8% (w/w) aqueous colloidal dispersion having an EW of 999.

[0111] 3.33g DE1021 Nafion® was dripped into a 500 mL round bottom flask containing 196.67g Baytron-P® CH8000 while being stirred with a magnetic stirrer. It took about 30 minutes to complete the addition. The mixture was left stirred for 4 hours and was then transferred to a 250 mL plastic bottle. Resulting dispersion contained 2.94% solid in which the equivalent ratio between Nafion® /PEDT/PSSA was 0.2/1.0/15.4. The entire dispersion was then subjected to sonication using an Ultrasonic Processor XL (Heat Systems, Inc., Farmingdale, NY, USA) set at power 7 for total 30 seconds "On" time (15 seconds On/ 15 seconds Off). It was sonicated one more time using the same conditions. The dispersion was then checked for particle size using an AccuSizer Model 780A (Particle Sizing Systems, Santa Barbara, CA). Particle size count ("PSC") was 31,302 particles in one mL of dispersion with particles greater than 1.51 μm. Prior to sonication, PSC was 113,760.

[0112] The entire sonicated dispersion was divided into two portions, ~100g each. The as-sonicated portion ("Sample 12a"), without adjustment of pH, had a pH of 1.4 and conductivity of $3.3x10^{-6}$S/cm, which was lower than the conductivity of the starting material (~10^{-5}S/cm).

[0113] The other half portion was run through a 100 mL column packed with 15g of Monoplus S100 on the bottom and 15g of MP 62 WS on the top. Monoplus S100 is a trade name from Bayer GmbH (Pittsburgh, PA) for sodium sulfonate of crosslinked polystyrene, cation exchange resin. MP62 WS is a trade from Bayer for free base/chloride of tertiary/quaternary amine of crosslinked polystyrene, anion exchange resin. The two resins were washed first before use with deionized water separately until there was no color in the water. The pH of the resin-treated sample (12b) was 3.7, and the conductivity was $2.3x10^{-6}$/cm. Particle size count ("PSC") was 27,275 particles in one mL of dispersion with particles greater than 1.51 μm.

[0114] The two samples of Baytron-P®/Nafion® blends were then tested for device performance. Each was spun on glass/ITO substrates (30mmx30mm) having ITO thickness of 100 to 150nm and 15mm x 20mm ITO area for light emission backlight substrates, and baked at 200°C in air for 5 minutes. The thickness of the buffer layer is given in Table 7 below. For the light-emitting layer, a 1% (w/v) toluene solution of Lumination Green from Dow Chemicals (Midland, MI) was spin-coated on top of the buffer layer films to a thicknes of ~700 Å, and subsequently baked at 180°C in a dry box for 10 minutes. Immediately after, a 3 nm thick barium layer and a 300-500 nm aluminum layer were deposited on the Lumination Green films to serve as a cathode. The device data summarized in Table 8 clearly shows that the device made with the Baytron-P®/Nafion® blend with a higher pH (3.8 vs. 1.4) has a lower voltage, and higher efficiency at 1,000cd/m2 and 25°C.

Table 8

Device Performance at 1,000cd/m^2 and 25°C.		
Buffer	Sample 12a pH=1.4	Sample 12b pH=3.7
Efficiency (cd/A)	6.4	14
Voltage (V)	3.6	3
Buffer Thickness (A)	946	885
Conductivity (S/cm)	$3.3x10^{-6}$S/cm	$2.3x10^{-6}$S/cm

Example 13 (REFERENCE)

[0115] This example illustrates the blending of a higher percentage of Nafion® with Baytron-P® CH8000 by sonication, the re-dispersibility of dried solids in water, and ion exchange resin treatment for achieving high pH and improved device performance.

[0116] In this example, Baytron-P® CH8000 (Lot# BPSS0007, solid:2.8%; pH~1.7) was used to form a blend with Nafion®. The Nafion® used for the polymerization is DE1021, a commercial grade of Nafion®. It is 11.8% (w/w) aqueous colloidal dispersion having an EW of 999.

[0117] 15.59g DE1021 Nafion® was dripped into a 500 mL round bottom flask containing 184.40g Baytron-P® CH8000 while being stirred with a magnetic stirrer. It took about 30 minutes to complete the addition. The mixture was left stirred for 4 hours and was then transferred to a 250 mL plastic bottle. Resulting dispersion contains 3.45% solids in which the equivalent ratio between Nafion® /PEDT/PSSA was 1.0/1.0/15.4. The entire dispersion was then subjected to sonication using an Ultrasonic Processor XL (Heat Systems, Inc., Farmingdale, NY, USA) set at power 7 for total 30 seconds "On" time (15 seconds On/ 15 seconds Off). It was sonicated one more time using the same conditions. The dispersion was then checked for particle size using an AccuSizer Model 780A (Particle Sizing Systems, Santa Barbara, CA). Particle size count ("PSC") was 83,227 particles in one mL of dispersion with particles greater than 1.51 μm. Prior to sonication, PSC was 745,311.

[0118] The entired sonicated dispersion was divided into two portions, ~100g each. The as-sonicated portion ("Sample 13a"), without adjustment of pH, had a pH of 1.4 and conductivity of $2.0x10^{-6}$S/cm, which was lower than the conductivity of the starting material (~10^{-5}S/cm). A few drops of the aqueous dispersion was placed on a microscope slide for drying at room temperature in inert atmosphere. The dried solids were readily re-dispersible in water as soon as they were immersed in the water.

[0119] The other half portion was ran through a 100 mL column packed with 15g of Monoplus S100 on the bottom and 15g of MP 62 WS on the top. Monoplus S100 is a trade name from Bayer GmbH (Pittsburgh, PA) for sodium sulfonate of crosslinked polystyrene, cation exchange resin. MP62 WS is a trade from Bayer for free base/chloride of tertiary/quaternary amine of crosslinked polystyrene, anion exchange resin. The two resins were washed first before use with deionized water separately until there was no color in the water. The pH of the resin-treated sample (13b) was 3.8, and the conductivity was 2.7×10^{-6}S/cm.

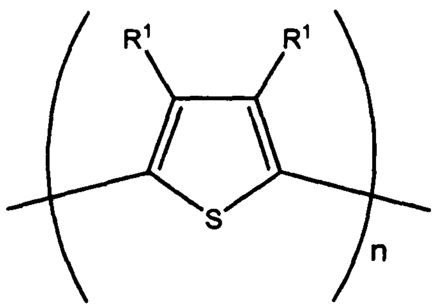
[0120] The two samples of Baytron-P/Nafion® blends were then tested for device performance. Each was spun on glass/ITO substrates (30mmx30mm) having ITO thickness of 100 to 150nm and 15mm x 20mm ITO area for light emission backlight substrates and baked at 200°C in air for 5 minutes. Thickness of the buffer layer is given in Table 8 below. For the light-emitting layer, a 1% (w/v) toluene solution of Lumination Green from Dow Chemicals (Midland, MI) was spin-coated on top of the buffer layer films to a thicknes of ~700 Å, and subsequently baked at 180°C in dry box for 10 minutes. Immediately after, a 3 nm thick barium layer and a 300-500 nm aluminum layer were deposited on the Lumination Green films to serve as a cathode. The device data summarized in Table 9 clearly shows that the device made with a Baytron-P®/Nafion® blend with a higher pH (3.8 vs. 1.4) has a lower voltage and higher efficiency at 1,000cd/m2 and 25°C.

Table 9

Device Performance at 1,000cd/m^2 and 25°C.		
Buffer	Sample 13a pH=1.4	Sample 13b pH=3.8
Efficiency (cd/A)	10.6	13.9
Voltage (V)	3.6	3.2
Buffer Thickness (A)	941	796
Conductivity (S/cm)	2.0×10^{-6}S/cm	2.7×10^{-6}S/cm

Claims

1. A composition comprising an aqueous dispersion of an electrically conductive organic polymer selected from the group consisting of polythiophenes of Formula III, polypyrroles of Formula IV, and combinations thereof, doped with a polymeric acid and a plurality of nanoparticles, wherein Formula III is:

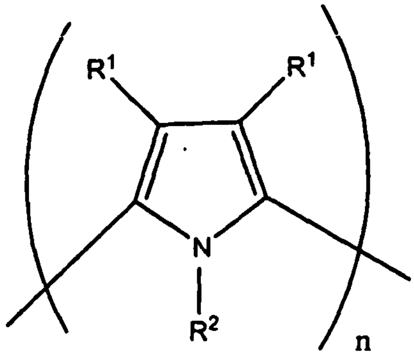


(III)

wherein:

R^1 is independently selected so as to be the same or different at each occurrence and is selected from alkyl, alkenyl, alkanoyl, alkythio, aryloxy, alkylthioalkyl, alkylaryl, arylalkyl, amino, alkylamino, dialkylamino, aryl, alkylsulfinyl, alkoxyalkyl, alkylsulfonyl, arylthio, arylsulfinyl, alkoxycarbonyl, arylsulfonyl, acrylic acid, phosphoric acid, phosphonic acid, halogen, nitro, cyano, hydroxyl, epoxy, silane, siloxane, alcohol, amidosulfonate, benzyl, carboxylate, ether, ether carboxylate, ether sulfonate, sulfonate, sulfonate, and urethane; or both R^1 groups together may form an alkenylene chain completing a 3, 4, 5, 6, or 7-membered aromatic or alicyclic ring, which

ring may optionally include one or more divalent nitrogen, or sulfur atoms, and n is at least 4; or both R^1 together form -O-$(CHY)_m$-O-, where m is 2 or 3, and Y is the same or different at each occurrence and is selected from hydrogen, alkyl, alcohol, amidosulfonate, benzyl, carboxylate, ether, ether carboxylate, ether sulfonate, sulfonate, sulfonate, and urethane, wherein at least one Y group is a substituent having F substitute for at least one hydrogen;
and Formula IV is:



(IV)

wherein:

n is at least about 4;
R^1 is independently selected so as to be the same or different at each occurrence and is selected from hydrogen, alkyl, alkenyl, alkoxy, alkanoyl, alkythio, aryloxy, alkylthioalkyl, alkylaryl, arylalkyl, amino, alkylamino, dialkylamino, aryl, alkylsulfinyl, alkoxyalkyl, alkylsulfonyl, arylthio, arylsulfinyl, alkoxycarbonyl, arylsulfonyl, acrylic acid, phosphoric acid, phosphonic acid, halogen, nitro, cyano, hydroxyl, epoxy, silane, siloxane, alcohol, amidosulfonate, benzyl, carboxylate, ether, ether carboxylate, ether sulfonate, sulfonate, sulfonate, and urethane; or both R^1 groups together may form an alkylene or alkenylene chain completing a 3, 4, 5, 6, or 7-membered aromatic or alicyclic ring, which ring may optionally include one or more divalent nitrogen, sulfur or oxygen atoms; and
R^2 is independently selected so as to be the same or different at each occurrence and is selected from hydrogen, alkyl, alkenyl, aryl, alkanoyl, alkylthioalkyl, alkylaryl, arylalkyl, amino, epoxy, silane, siloxane, alcohol, amidosulfonate, benzyl, carboxylate, ether, ether carboxylate, ether sulfonate, sulfonate, and urethane,

characterised in that said nanoparticles are colloid-forming fluorinated polymeric sulfonic acid particles.

2. A composition according to Claim 1, wherein the pH of the composition is between 1 and 8.

3. A composition according to Claim 1, wherein said nanoparticle is a perfluoroethylene sulfonic acid.

4. A composition according to Claim 1, wherein said nanoparticles have a particle size less than about 500 nm.

5. A composition according to Claim 1, wherein said nanoparticles have a particle size less than about 250 nm.

6. A composition according to Claim 1, wherein said nanoparticles have a particle size less than about 50 nm.

7. A composition according to Claim 1, wherein said colloid-forming fluorinated polymeric sulfonic acid comprises a polymer having a carbon backbone and side chains represented by the formula

$$-(O\text{-}CF_2CFR_f)_a\text{-}O\text{-}CF_2CFR'_fSO_3X$$

wherein:

a is 0, 1 or 2;
R_f and R'_f are independently selected from F, Cl or a perfluorinated alkyl group haing 1 to 10 carbon atoms; and
X is H, Li, Na, K or $N(R^1)(R^2)(R^3)(R^4)$ and R^1, R^2, R^3 and R^4 are the same or different and are selected from

H, CH_3 and C_2H_5;

and wherein at least 50% of the total number of hydrogen and halogen atoms on the carbon backbone are fluorine atoms.

8. A method of forming a buffer layer in an electronic device, said method comprising depositing a buffer layer from the aqueous dispersion of claim 1 onto a substrate.

9. The method according to Claim 8 wherein said nanoparticles comprise perftuoroethylene sulfonic acid.

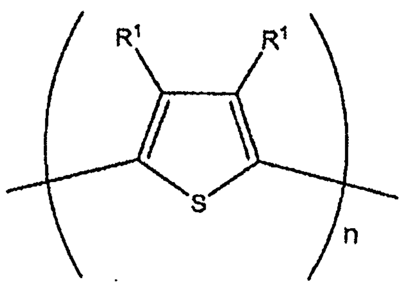
10. The method according to Claim 8, wherein said layer has a conductivity of less than about 1 x 10^{-3} S/cm.

11. The method according to Claim 8, wherein said layer has a conductivity of less than about 1 x 10^{-5} S/cm.

12. The method according to claim 8, wherein the electronic device is an organic electronic device. .

Patentansprüche

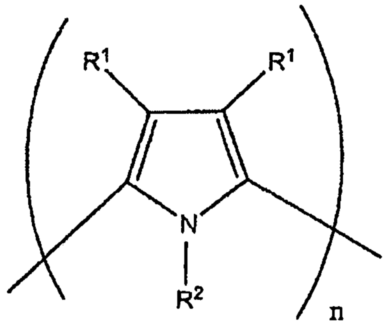
1. Zusammensetzung, die eine wäßrige Dispersion eines elektrisch leitenden organischen Polymers aufweist, das aus der Gruppe ausgewählt ist, die aus Polythiophenen gemäß Formel III, Polypyrrolen gemäß Formel IV und Kombinationen davon besteht, dotiert mit einer polymeren Säure und einer Vielzahl von Nanoteilchen, wobei Formel III durch



(III)

gegeben ist, wobei:

R^1 unabhängig voneinander bei jedem Auftreten gleich oder verschieden ausgewählt ist und unter Alkyl-, Alkenyl-, Alkanoyl-, Alkylthio-, Aryloxy-, Alkylthioalkyl-, Alkylaryl-, Arylalkyl-, Amino-, Alkylamino-, Dialkylamino-, Aryl-, Alkylsulfinyl-, Alkoxyalkyl-, Alkylsulfonyl-, Arylthio-, Arylsulfinyl-, Alkoxycarbonyl-, Arylsulfonyl-, Acrylsäure-, Phosphorsäure-, Phosphonsäure-, Halogen-, Nitro-, Cyano-, Hydroxyl-, Epoxy-, Silan-, Siloxan-, Alkohol-, Amidosulfonat-, Benzyl-, Carboxylat-, Ether-, Ethercarboxylat-, Ethersulfonat-, Sulfonat- und Urethan-Komponenten ausgewählt ist; oder beide R^1-Gruppen zusammen eine Alkenylenkette bilden können, die einen 3-, 4-, 5-, 6- oder 7-gliedrigen aromatischen oder alicyclischen Ring schließt, wobei der Ring wahlweise ein oder mehrere zweiwertige Stickstoff- oder Schwefelatome enthalten kann; und n mindestens gleich 4 ist; oder beide R^1-Gruppen zusammen -O-$(CHY)_m$-O- bilden, wobei m gleich 2 oder 3 ist und Y bei jedem Auftreten gleich oder verschieden ist und unter Wasserstoff-, Alkyl-, Alkohol-, Amidosulfonat-, Benzyl-, Carboxylat-, Ether-, Ethercarboxylat-, Ethersulfonat-, Sulfonat- und Urethan-Komponenten ausgewählt ist, wobei die mindestens eine Y-Gruppe ein Substituent ist, in dem mindestens ein Wasserstoff durch F substituiert ist;
und wobei Formel IV durch



(IV)

gegeben ist, wobei:

R^1 unabhängig voneinander bei jedem Auftreten gleich oder verschieden ausgewählt ist und unter Wasserstoff-, Alkyl-, Alkenyl-, Alkoxy-, Alkanoyl-, Alkylthio-, Aryloxy-, Alkylthioalkyl-, Alkylaryl-, Arylalkyl-, Amino-, Alkylamino-, Dialkylamino-, Aryl-, Alkylsulfinyl-, Alkoxyalkyl-, Alkylsulfonyl-, Arylthio-, Arylsulfinyl-, Alkoxycarbonyl-, Arylsulfonyl-, Acrylsäure-, Phosphorsäure-, Phosphonsäure-, Halogen-, Nitro-, Cyano-, Hydroxyl-, Epoxy-, Silan-, Siloxan-, Alkohol-, Amidosulfonat-, Benzyl-, Carboxylat-, Ether-, Ethercarboxylat-, Ethersulfonat-, Sulfonat- und Urethan-Komponenten ausgewählt ist; oder beide R^1-Gruppen zusammen eine Alkylen- oder Alkenylenkette bilden können, die einen 3-, 4-, 5-, 6- oder 7-gliedrigen aromatischen oder alicyclischen Ring schließt, wobei der Ring wahlweise ein oder mehrere zweiwertige Stickstoff-, Schwefel- oder Sauerstoffatome enthalten kann; und
R^2 unabhängig voneinander bei jedem Auftreten gleich oder verschieden ausgewählt ist und unter Wasserstoff-, Alkyl-, Alkenyl-, Aryl-, Alkanoyl-, Alkylthioalkyl-, Alkylaryl-, Arylalkyl-, Amino-, Epoxy-, Silan-, Siloxan-, Alkohol-, Amidosulfonat-, Benzyl-, Carboxylat-, Ether-, Ethercarboxylat-, Ethersulfonat-, Sulfonat- und Urethan-Komponenten ausgewählt ist,
dadurch gekennzeichnet, daß die Nanoteilchen kolloidbildende fluorierte polymere Sulfonsäureteilchen sind.

2. Zusammensetzung nach Anspruch 1, wobei der pH-Wert der Zusammensetzung zwischen 1 und 8 liegt.

3. Zusammensetzung nach Anspruch 1, wobei die Nanoteilchen aus einer Perfluorethylensulfonsäure bestehen.

4. Zusammensetzung nach Anspruch 1, wobei die Nanoteilchen eine Teilchengröße von weniger als etwa 500 nm aufweisen.

5. Zusammensetzung nach Anspruch 1, wobei die Nanoteilchen eine Teilchengröße von weniger als etwa 250 nm aufweisen.

6. Zusammensetzung nach Anspruch 1, wobei die Nanoteilchen eine Teilchengröße von weniger als etwa 50 nm aufweisen.

7. Zusammensetzung nach Anspruch 1, wobei die kolloidbildende fluorierte polymere Sulfonsäure ein Polymer mit einer Kohlenstoffhauptkette und Seitenketten aufweist, das durch die Formel

$$-(O-CF_2CFR_f)_a-O-CF_2CFR'_fSO_3X$$

dargestellt wird, wobei:

a gleich 0, 1 oder 2 ist;
R_f und R'_f unabhängig voneinander unter F, Cl oder einer perfluorierten Alkylgruppe mit 1 bis 10 Kohlenstoffatomen ausgewählt sind; und
X für H, Li, Na, K oder $N(R^2)(R^2)(R^3)(R^4)$ steht und R^1, R^2, R^3 und R^4 gleich oder verschieden und unter H, CH_3 und C_2H_5 ausgewählt sind;
und wobei mindestens 50% der Gesamtzahl an Wasserstoff- und Halogenatomen an der Kohlenstoffhauptkette Fluoratome sind.

8. Verfahren zur Bildung einer Pufferschicht in einem elektronischen Bauelement, wobei das Verfahren die Abscheidung einer Pufferschicht aus der wäßrigen Dispersion nach Anspruch 1 auf ein Substrat aufweist.

9. Verfahren nach Anspruch 8, wobei die Nanoteilchen Perfluorethylensulfonsäure aufweisen.

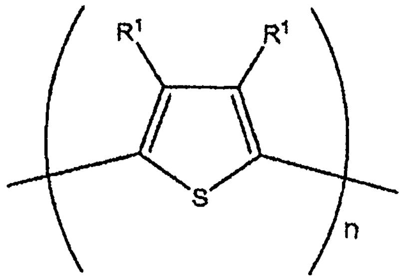
10. Verfahren nach Anspruch 8, wobei die Schicht eine Leitfähigkeit von weniger als etwa 1×10^{-3} S/cm aufweist.

11. Verfahren nach Anspruch 8, wobei die Schicht eine Leitfähigkeit von weniger als etwa 1×10^{-5} S/cm aufweist.

12. Verfahren nach Anspruch 8, wobei das elektronische Bauelement ein organisches elektronisches Bauelement ist.

Revendications

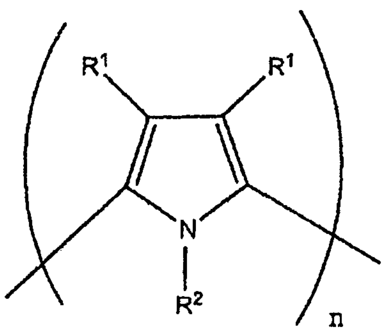
1. Composition comprenant une dispersion aqueuse d'un polymère organique électriquement conducteur choisi parmi le groupe constitué des polythiophènes de formule III, polypyrroles de formule IV, et des combinaisons de ceux-ci, dopé avec un acide polymère et une pluralité de nanoparticules, dans laquelle la formule III est :



(III)

dans laquelle :

R^1 est indépendamment choisi afin d'être identique ou différent à chaque occurrence et est choisi parmi les groupes alkyle, alcényle, alcanoyle, alkylthio, aryloxy, alkylthioalkyle, alkylaryle, arylalkyle, amino, alkylamino, dialkylamino, aryle, alkylsulfinyle, alcoxyalkyle, alkylsulfonyle, arylthio, arylsulfinyle, alcoxycarbonyle, arylsulfonyle, acide acrylique, acide phosphorique, acide phosphonique, halogéno, nitro, cyano, hydroxyle, époxy, silane, siloxane, alcool, sulfonate d'amide, benzyle, carboxylate, éther, carboxylate d'éther, sulfonate d'éther, sulfonate, et uréthane ; où les deux groupes R^1 conjointement peuvent former une chaîne alcénylène complétant un cycle aromatique ou alicyclique à 3, 4, 5, 6 ou 7 chaînons, lequel cycle peut optionnellement inclure un ou plusieurs atome(s) d'azote divalent, ou atome(s) de soufre, et n prend au moins la valeur de 4 ; ou
les deux R^1 conjointement forment $-O-(CHY)_m-O-$, où m prend la valeur de 2 ou 3, et Y est identique ou différent à chaque occurrence et est choisi parmi les groupes hydrogéno, alkyle, alcool, sulfonate d'amide, benzyle, carboxylate, éther, carboxylate d'éther, sulfonate d'éther, sulfonate, et uréthane, dans laquelle au moins un groupe Y est un substituant ayant le substitut F pour au moins un atome d'hydrogène ;
et la formule IV est :



(IV)

dans laquelle :

n a au moins la valeur d'environ 4 ;

R^1 est indépendamment choisi afin d'être identique ou différent à chaque occurrence et est choisi parmi un groupe hydrogéno, alkyle, alcényle, alcoxy, alcanoyle, alkythio, aryloxy, alkylthioalkyle, alkylaryle, arylalkyle, amino, alkylamino, dialkylamino, aryle, alkylsulfinyle, alcoxyalkyle, alkylsulfonyle, arylthio, arylsulfinyle, alcoxycarbonyle, arylsulfonyle, acide acrylique, acide phosphorique, acide phosphonique, halogéno nitro, cyano, hydroxyle, époxy, silane, siloxane, alcool, sulfonate d'amide, benzyle, carboxylate, éther, carboxylate d'éther, sulfonate d'éther, sulfonate, et uréthane ; ou les deux groupes R^1 conjointement peuvent former une chaîne alcylène ou alcénylène complétant un cycle aromatique ou alicyclique de 3, 4, 5, 6 ou 7 chaînons, lequel cycle peut optionnellement inclure un ou plusieurs atome(s) d'azote divalent, atome(s) de soufre ou d'oxygène ; et

R^2 est indépendamment choisi afin d'être identique ou différent à chaque occurrence et est choisi parmi un groupe hydrogéno, alkyle, alcényle, aryle, alcanoyle, alkylthioalkyle, alkylaryle, arylalkyle, amino, époxy, silane, siloxane, alcool, sulfonate d'amide, benzyle, carboxylate, éther, carboxylate d'éther, sulfonate d'éther, sulfonate et uréthane,

caractérisée en ce que lesdites nanoparticules sont des particules d'acide sulfonique polymère fluoré formant des colloïdes.

2. Composition selon la revendication 1, dans laquelle le pH de la composition est compris entre 1 et 8.

3. Composition selon la revendication 1, dans laquelle ladite nanoparticule est un acide perfluoroéthylène sulfonique.

4. Composition selon la revendication 1, dans laquelle lesdites nanoparticules ont une taille de particule inférieure à environ 500 nm.

5. Composition selon la revendication 1, dans laquelle lesdites nanoparticules ont une taille de particule inférieure à environ 250 nm.

6. Composition selon la revendication 1, dans laquelle lesdites nanoparticules ont une taille de particule inférieure à environ 50 nm.

7. Composition selon la revendication 1, dans laquelle ledit acide sulfonique polymère fluoré formant colloïde comprend un polymère ayant un squelette carboné et des chaînes latérales représentées par la formule

$$-(O\text{-}CF_2CFR_f)_a\text{-}O\text{-}CF_2CFR'_fSO_3X$$

dans laquelle :

a a la valeur de 0, 1 ou 2 ;

R_f et R'_f sont indépendamment choisis parmi F, Cl ou un groupe alkyle perfluoré ayant 1 à 10 atome(s) de carbone ; et

X est H, Li, Na, K ou $N(R^1)(R^2)(R^3)(R^4)$ et R^1, R^2, R^3 et R^4 sont identiques ou différents et sont choisis parmi H, CH_3 et C_2H_5 ;

et dans laquelle au moins 50 % du nombre total d'atomes d'hydrogène et d'halogène sur le squelette carboné sont des atomes de fluor.

8. Procédé de formation d'une couche tampon dans un dispositif électronique, ledit procédé comprenant le dépôt d'une couche tampon à partir de la dispersion aqueuse selon la revendication 1 sur un substrat.

9. Procédé selon la revendication 8, dans lequel lesdites nanoparticules comprennent de l'acide perfluoroéthylène sulfonique.

10. Procédé selon la revendication 8, dans lequel ladite couche a une conductivité inférieure à environ 1×10^{-3} S/cm.

11. Procédé selon la revendication 8, dans lequel ladite couche a une conductivité inférieure à environ 1×10^{-5} S/cm.

12. Procédé selon la revendication 8, dans lequel le dispositif électronique est un dispositif électronique organique.

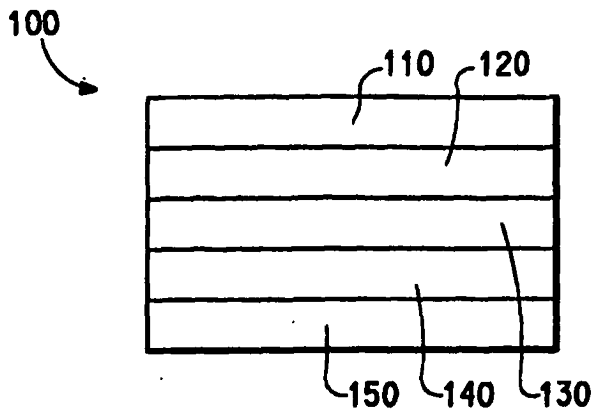


FIG. 1

REFERENCES CITED IN THE DESCRIPTION

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专利名称(译)	导电有机聚合物/纳米颗粒复合物及其使用方法		
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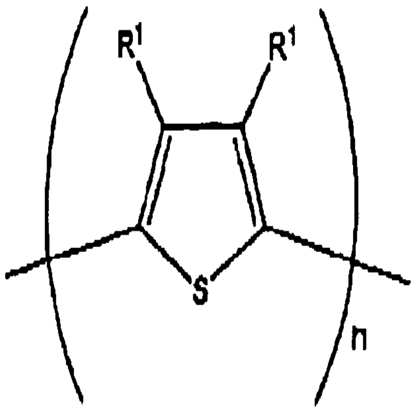
摘要(译)

提供了包含导电有机聚合物的水分散体和多个纳米颗粒的组合物，其中可以调节pH以改善有机电子器件性能。由本发明组合物沉积的薄膜可用作电致发光器件中的缓冲层，例如有机发光二极管（OLED）和用于薄膜场效应晶体管的电极。含有纳米颗粒的缓冲层可以具有比没有纳米颗粒的缓冲层低得多的导电率另外，当结合到电致发光（EL）器件中时，根据本发明的缓冲层有助于EL器件的更高的应力寿命。



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