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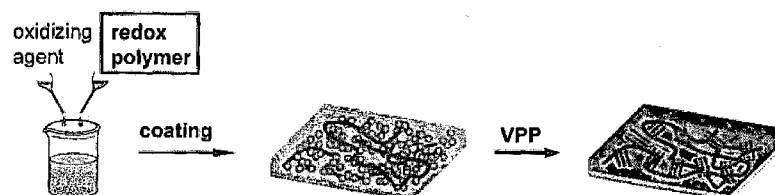
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(54) Title: CONDUCTING POLYMER / REDOX POLYMER BLENDS VIA IN-SITU OXIDATIVE POLYMERIZATION - PRE-
 PARATION METHODS AND APPLICATION AS AN ELECTRO-ACTIVE POLYMERIC MATERIALS

[Fig. 1]



(57) Abstract: The composition is made as follows. Firstly, the PTAm/Fe(III)(OTs)₃ solution was spin-coated onto substrates, glass slides and silicon wafers at 1200 rpm. Then the samples were thereafter dried for 60 seconds at 70°C (in oven) before transferred to the VPP chamber. The VPP chamber was a closed glass container with 0.1ml of EDOT monomer in an open Petri desk in the bottom. The VPP chamber was preheated to 70°C before the samples were transferred. After 30 min at 70°C the PEDOT polymerization was completed and the samples were removed from the VPP chamber and after cooling to room temperature, washed in ethanol to remove Fe(II) and excess of (OTs)₃ anions. After drying in air the samples were used for electrochemical testing and fabrication of electrochemical cells.

Description

Title of Invention: Conducting Polymer / Redox Polymer Blends via in-situ Oxidative Polymerization - Preparation Methods and Application as an Electro-active Polymeric Materials

Technical Field

[0001] The present invention relates generally to electro-active polymer blends. In particular, the invention relates to a method of preparing an intrinsically conducting polymer in presence of redox polymers, a method of forming the intrinsically conducting and redox-active polymer on a surface of a substrate, a composition for preparing the intrinsically conducting and redox-active polymer. The obtained materials may be used for electrochemical applications such as energy-storage devices comprising the intrinsically conducting polymer / redox polymer composites and for electro-catalytic materials.

Background Art

[0002] Although a PEDOT/PSS suspension shows excellent film forming properties, the obtained film does not express the full possibilities of PEDOT in terms of conductivity. Previously, we have shown that vapor phase polymerization (VPP) can be used for in-situ polymerization of EDOT inside a number of different non-conducting polymers and rubbers, and to give polymer composite with high conductivity.

[0003] Redox polymers comprising of non-conducting polymers with redox-active groups, have been widely used as redox catalysts and electro-active materials. In particular, we have utilized the “radical polymer” as electrode-active material in a rechargeable battery. Radical polymers bearing robust but redox-active radical groups, can be adopted as cathode- and anode-active materials. The energy-storage device composed of these polymer electrodes exhibited an extremely high power-rate performance.

[0004] A combination of conducting polymers and redox polymers are promising to

give electro-active materials for various electronics and catalytic applications, however, there have been few reports on preparation of composite materials due to the solubility issues. There are some reports on conducting polymers bearing redox-active groups, such as polyanilines bearing disulfide redox couples as side groups (E. Tsuchida, *Macromolecules*, 2001, 34, 2751; P. J. Skabara, et al., *J. Phys. Chem. B.*, 2006, 110, 3140). However, such functional polymers exhibited capacitive redox behavior and low conductivity.

Summary of Invention

[0005] In this invention, we utilized, for the first time, chemical oxidative polymerization of (EDOT) in presence of redox polymers to prepare the composite materials. We optimized the composition of solvents, oxidants, and organic bases, substrates, coating conditions, and reaction conditions. Polymer composite materials comprising PEDOT and redox polymers were successfully obtained. In some cases, radical group, i.e. nitroxide, in the redox polymers was transformed to unreactive groups, i.e. oxoammonium salts because the radical inhibits the oxidative polymerization.

[0006] Advantages of this preparation method are: to maintain high conductivity of PEDOT in the composite; to well-disperse two polymers in the blend, overcoming solubility issues; and to modulate the redox potential of PEDOT in presence of redox polymers.

[0007] Examples of the outcomes of the PEDOT/redox polymer composites are: electrode-active material in for energy-storage devices such as rechargeable battery; electro-active components for solar cell applications; and catalysts for oxygen reduction in the water-splitting process and in fuel cells.

[0008] According to an embodiment of the present invention, there is provided a method for the preparation of composite material comprising of conducting polymer and redox-active molecule.

[0009] Further, there is provided a method for the preparation of a polymer blend material comprising of conducting polymer and redox polymer.

[0010] For example, the method is based on oxidative polymerization of the conducting polymer; the method is based on vapor-phase oxidative polymerization of the conducting polymer; the vapor-phase polymerization is carried out in presence of redox polymers; redox polymers are radical polymers, their precursors, and charged polymers; radical polymers are characterized as the non-conducting polymer bearing robust but redox-active organic groups such as nitroxides, galvinoxyl, nitronylnitroxide; radical groups are transformed into unreactive group for in-situ oxidative polymerization; radical precursor polymers are used for in-situ vapor-phase polymerization without any treatment, and the radical generation was carried out chemically or electrochemically after preparing composites; the charged polymers are characterized as the non-conducting polymer bearing redox-active charged group such as viologen; the obtained conducting polymer/redox polymer composite is utilized as electrode-active material in a battery or a photovoltaic cell; the obtained conducting polymer/redox polymer composite is utilized as electro-catalyst; the obtained conducting polymer/redox polymer composite is utilized as electro-catalyst for oxygen reduction, water splitting, decomposition of sulfur dioxide, and oxidation reaction for fuel-cells.

[0011] Other features and advantages of the present invention will become apparent from the following detailed description, taken in conjunction with the accompanying drawings, which illustrate, by way of example, the principles of the invention.

Brief Description of Drawings

[0012] FIG. 1 is a drawing illustrating a method of applying vapor-phase polymerization of thiophene in presence of redox polymer.

[0013] FIG. 2 is a drawing showing a schematic battery configuration utilizing the redox polymer / conducting polymer composite electrodes.

[0014] FIG. 3 is a graph showing an investigation result about composition dependence of PEDOT/PTAm on the charge/discharge behavior.

[0015] FIG. 4 is a graph showing an investigation result about composition dependence of PEDOT/PTAm on the charge/discharge behavior.

[0016] FIG. 5 is a graph showing an investigation result of a rechargeable battery having a cathode of the present invention and a conventional lithium-ion rechargeable battery.

[0017] FIG. 6 is a drawing showing illustrating a method of manufacturing a configuration for a solar power generation.

[0018] FIG. 7 is a graph showing an investigation result of light vs. dark GALVI 1 PEDOT 1 PTHF 1 - SO₂ conversion for gas cell.

Description of Embodiments

[0019] Fig. 1 and 2 show examples of the present invention.

[0020] I) Preparation of PEDOT / PTAm blends by VPP

a) Preparation of PTAm / Fe(III)(OTs)₃ solution

For every radical polymer / oxidant combination a common solvent or solvent mixture have to be selected. In case of PTAm/Fe(III)(OTs)₃ a 4:1 mixture of acetic acid and water was found to be an adequate solvent. For other combination of the mixed solvents, water/acetonitrile/tetrahydrofuran (1/2/3 v/v/v) can be utilized. The ratio between conducting polymer and radical polymer (i.e. PEDOT and PTAm) is determined by the ratio between PTAm and oxidant (Fe(III)(OTs)₃), as the amount of oxidant will determine the amount of PEDOT polymerized during the Vapor Phase Polymerization. The amount of PEDOT is dictated by the oxidative polymerization mechanism which requires approximately 2.25 mol Fe(III) to produce 1 mol of oxidized PEDOT. This implies that 1g of Fe(III)(OTs)₃ will produce 0.14g of oxidized PEDOT, which is ca. 0.1ml of PEDOT. From this follows that for obtaining a 1:1 volumetric mixture and PEDOT and PTAm in the final product, 0.1ml of PTAm have to be added to 1g of Fe(III)(OTs)₃ in the acetic acid / water mixture. In practice, 5ml of acetic acid / water mixture was heated to 40° C with stirring, 0.1ml of PTAm was added and stirred for 1 min to secure solution of the polymer. Hereafter 1g of Fe(III)(OTs)₃ was added slowly under stirring and further stirred for 2 min (with closed lid) to obtain a typical orange-red solution. The mixture was cooled to room-temperature before used for vapor phase polymerization.

[0021] b) Vapour Phase Polymerization of PEDOT/PTAm

The PTAm/Fe(III)(OTs)₃ solution was spin-coated onto substrates like gold-coated mylar®, glass slides and silicon wafers at 1200 rpm. The samples were thereafter dried for 60 seconds at 70°C (in oven) before transferred to the VPP chamber. The VPP chamber was a closed glass container with 0.1ml of EDOT monomer in an open Petri desk in the bottom. The VPP chamber was preheated to 70°C before the samples were transferred. After 30 min at 70°C the PEDOT polymerization was completed and the samples were removed from the VPP chamber and after cooling to room temperature, washed in ethanol to remove Fe(II) and excess of (OTs)₃ anions. After drying in air the samples were used for electrochemical testing and fabrication of electrochemical cells.

[0022] c) Multilayer deposition

The procedure described in b) can produce PEDOT/PTAm coatings with thicknesses in the range of 500 to 1200 nm depending on e.g. spin-coating speed. For practical devices much thicker layers are required in order to obtain sufficient electrochemical capacity. For this purpose a multi-layer technique can be used, where the spin-coating of PTAm/Fe(III)(OTs)₃ followed by VPP is repeated several times before the final washing and drying step. The obtained films after five times gave 5µm thickness.

[0023] II) Preparation of PEDOT / PTAm blends by casting from solution

This procedure is providing the possibility of producing PEDOT/PTAm material in larger quantities without the disadvantage of multilayer deposition. The preparation of the PTAm/Fe(III)(OTs)₃ solution is similar to procedure described above under example Ia), however the mixture is cooled to 0°C after addition of the oxidant. The 5ml cooled and stirred mixture is added 0.07ml pyridine as basic inhibitor, followed by 0.1ml EDOT monomer. The obtained mixture has a pot-life of about 1 hour at 0°C before precipitates of PEDOT is starting to form. This reactive mixture can be cast on various substrates, conducting as well as non-conducting. After casting, the main part of the solvent is evaporated at 40°C on a hotplate or in an oven. Hereafter the temperature is raised to 70°C to initiate the polymerization of PEDOT. The polymerization time is around 40 min depending on the thickness of the layers. After polymerization, the samples were washed 3 times in ethanol for 30 min to remove residual Fe(II), Fe(III) and (OTs)₃ anions ions.

[0024] III) Preparation of PEDOT / PTMA blends

A Fe(III)(OTs)₃ butanol solution (40 wt%, 0.2 g) was further diluted with butanol (1.8 mL), and a THF solution (3 mL) of PTMA (20 mg) and pyridine (6.5 mg) were added into the solution. The solution was spin-coated onto the glass substrate (1000 rpm, 10 sec), and the substrate was preheated on the hot plate at 60°C for 5 seconds. The substrate was transferred into the VPP chamber, and the VPP of EDOT was carried out at 70°C for 50 min. The sample was removed from VPP chamber and cooled down to the room temperature. After polymerization, the sample was washed with water/methanol (3/2 volume/volume) mixture to remove residual Fe(II), Fe(III), and OTs ions. The sample was dried at room temperature to give greenish yellow film.

[0025] IV) Preparation of PEDOT / PV10 blends

A Fe(III)(OTs)₃ butanol solution (40 wt%, 0.348 g) was further diluted with butanol (0.15 mL), and a methanol solution (1.5 mL) of PV10 (20 mg) was added into the solution. PV10 retards the VPP, so pyridine was not necessary. The solution was spin-coated onto the glass substrate (1000 rpm, 10 sec), and the substrate was preheated on the hot plate at 60°C for 5 seconds. The substrate was transferred into the VPP chamber, and the VPP of EDOT was carried out at 70°C for 50 min. The sample was removed from VPP chamber and cooled down to the room temperature. After polymerization, the sample was washed with water/methanol (3/2 volume/volume) mixture to remove residual Fe(II), Fe(III), and OTs ions. The sample was dried at room temperature to give dark blue film.

[0026] V) Preparation of poly(3,4-ethylenedioxyppyrole) (PEDOP) / PV10 blends

A Fe(III)(OTs)₃ butanol solution (40 wt%, 0.348 g) was further diluted with butanol (0.15 mL), and a methanol solution (1.5 mL) of PV10 (20 mg) was added into the solution. PV10 retards the VPP, so pyridine was not necessary. The solution was spin-coated onto the glass substrate (1000 rpm, 10 sec), and the substrate was preheated on the hot plate at 60°C for 5 seconds. The substrate was transferred into the VPP chamber, and the VPP of 3,4-ethylenedioxyppyrole (EDOP) was carried out at 70°C for 50 min. The sample was removed from VPP chamber and cooled down to the room temperature. After polymerization, the sample was washed with water/methanol (3/2 volume/volume) mixture to remove residual Fe(II), Fe(III), and OTs ions. The

sample was dried at room temperature to give dark blue film.

[0027] VI) Preparation of PEDOT / PGSt blends

A Fe(III)(OTs)₃ butanol solution (40 wt%, 0.2 g) was further diluted with butanol (1.8 mL), and a THF solution (3 mL) of PGSt (14 mg) and pyridine (5.53 mg) were added into the solution. The solution was spin-coated onto the glass substrate (1000 rpm, 10 sec), and the substrate was preheated on the hot plate at 60°C for 5 seconds. The substrate was transferred into the VPP chamber, and the VPP of EDOT was carried out at 70°C for 50 min. The sample was removed from VPP chamber and cooled down to the room temperature. After polymerization, the sample was washed with water/methanol (3/2 volume/volume) mixture to remove residual Fe(II), Fe(III), and OTs ions. The sample was dried at room temperature to give greenish yellow film.

[0028] Cyclic voltammogram for PEDOT/PTAm (1/1) film (thickness = 200 nm) in 0.1 M aqueous solution of sodium p-toluene sulfonate exhibited a reversible redox behavior at 0.62 V vs. Ag/AgCl. PEDOT/PGSt (2/1) and PEDOT/PV10 (2/1) also exhibited reversible redox behaviors at 0.1 and – 0.6 V vs. Ag/AgCl repeatedly.

[0029] PEDOT/PTAm composite electrode was also characterized in the organic-based electrolyte solution. As for the electrolyte, ethylene carbonate/diethyl carbonate (3/7 volume/volume) containing 1.0 M LiPF₆ was used. In the inert atmosphere or glove box, the composite electrode swollen with the electrolyte was stacked with polypropylene-based pore film and lithium disc anode to fabricate the test coin cell. The galvanostatic charging/discharging of the battery was carried out to evaluate the charge capacity. Discharge curve exhibited a plateau voltage of 3.5 V, and discharge capacity was 120 mAh/g. Cycle stability of the PEDOT/PTAm electrode in the range of 3.0 – 4.0 V was evaluated after 500 cycles, to be 83% of the initial discharge capacity.

[0030] Composition of PEDOT/redox polymer

The composition dependence of PEDOT/PTAm on the charge/discharge behavior was investigated. PEDOT/PTAm composite films (composition rate: 1/1, 1/3; thickness = 1 μm) were prepared via vapor-phase polymerization, and covered with pure PEDOT layer as current collector like the PEDOT/PTAm composite film illustrated in Fig. 1. The half-cell was fabricated using PEDOT/PTAm working electrode, platinum counter electrodes, and Ag/AgCl reference electrode. 0.1 M

acetonitrile solution of tetraethylammonium p-toluene sulfonate was used as an electrolyte solution. Galvanostatic discharge curves at different current densities (10–360 C rate, where the 1 C rate is defined as the current density at which the charging and discharging of the battery takes 1 h) exhibited a plateau voltage of 0.75 V vs. Ag/AgCl, and discharge capacity decreased with increasing current densities (see Fig. 3 and 4). The discharge capacity of PEDOT/PTAm (1/1) was maintained over 90% of the loading amount up to 240C rate. For PEDOT/PTAm (1/3) electrode, the discharge capacity was maintained up to 120C.

[0031] In the aforementioned embodiment and other embodiments, the composition may further comprise a non-conductive polymer selected from a group consisting of poly-ethylene glycol, dextran, and a mixture thereof. The non-conductive polymer can be contained in the solution with the radical polymer (PTAm, etc.) and the oxidant (Fe(III)(OTs)₃).

[0032] Comparison with conventional lithium-ion rechargeable battery

As illustrated in Fig. 5, a test to compare a rechargeable battery having a cathode of the present invention and a conventional lithium-ion rechargeable battery was conducted. The test cell was composed of PTAm cathode and carbon anode and 1 M ethylene carbonate/diethyl carbonate (3/7) solution of LiPF₆ as the electrolyte. The cell exhibited high current rate performance in a range of 5C to 1200C. On the other hand, for a conventional lithium-ion battery, the charge capacity decreased dramatically even at 3C rate.

[0033] VII) Cell fabrication and characterization

Two composite electrodes (PEDOT/PTAm and PEDOT/PGSt) were prepared on Au Mylar film or ITO/glass substrate, and stacked with a separator film (thickness 0.5 mm). An acetonitrile solution (1 M) of tetraethylammonium tosylate was injected into the cell, and the cell was sealed with photo-curing adhesives. Galvanostatic charge-discharging curves exhibit a plateau voltage of 0.75 V repeatedly. The charge/discharge capacities were 120 mAh/g for PEDOT/PTAm cathode, and 55 mAh/g for PEDOT/PGSt anode, which supported the quantitative redox reaction of the composite electrodes, respectively.

[0034] The composition provided on the electrode is composed to have an electric conductivity which is higher than 1 S/cm, or preferably higher than 10 S/cm. By

preparing the composition as described above, the target conductivity can be achieved.

[0035] Soluble fullerene derivatives (PCBM) or methylviologen derivatives (MVTFSI2) was selected as an electron acceptor, mixed with oxidant solution, and spin-coated on the ITO substrate. In-situ oxidative polymerization of EDOT at 70°C for 60 min, the formed layer was washed with methanol and water to remove the unreacted monomer and excess oxidant solution. PCBM and MVTFSI2 were durable under the polymerization condition.

[0036] For dedoping of PEDOT or other conducting polymers, hydrazine vapor or its aqueous/alcohol mixed solution was used. Ammonium hydroxide aqueous solution was also applicable as the reducing agent. Electrochemical dedoping also yielded the dedoped conjugated polymers.

[0037] Terthiophene monomer (m.p. 93-95°C) was also applied for in-situ oxidative polymerization. Oxidant solution containing Fe(OTs)₃ was spin-coated onto the ITO substrate, and the substrate was set in the chamber, where terthiophene vapor formed at 100°C. After 6 h, excess oxidant was removed off by washing with ethanol to yield the polythiophene film. In presence of PCBM or methylviologen, in-situ oxidative polymerization of terthiophene and the following chemical dedoping with hydrazine afforded the donor/acceptor mixed layer. The fluorescent emission from the polythiophene at 570 nm (excitation at 460 nm) was quenched with PCBM or methylviologen, which indicated the photo-induced charge-separation.

[0038] Photocurrent and open circuit potential were observed under 1 Sun irradiation (Fig. 6).

[0039] VIII) Light stimulated SO₂ oxidation on PEDOT/PGSt blends

PEDOT and PEDOT/PGSt blends were made including Poly(tetrahydrofuran) (PTHF), a non-conducting polymer well-known for good SO₂ diffusivity, as follows: Fe(III)(OTs)₃ butanol solution (40 wt%, 0.5 ml) was mixed with 12 mg PGSt and 12 mg PTHF (MW: 2000) dissolved in 0.5ml butanol. After mixing, 7μl pyridine was added. This oxidant mixture was coated onto gold-coated PTFE membrane (Goretex®), dried and exposed to EDOT vapour at 70degC for 40min to perform vapour phase polymerization. The resulting films were washed in water to remove Fe(II) and excess of OTs and thereafter allowed to dry in air.

[0040] The PEDOT/PTHF and PEDOT/PGSt/PTHF coated membranes were

mounted as gas-diffusion electrodes with a standard three electrode setup on the coated side of the membrane and a SO₂ gas supply (5% SO₂ in nitrogen) on the other side. Galvanometric measurements were performed at potentials from 0 to 0.6V vs SCE. The addition of PGSt to the PEDOT/PTHF blend resulted in a lower over-potential and higher conversion currents. When light (3000K) was shined on the PEDOT/PGSt/PTHF electrodes (see Fig. 7) there was a significant increase in conversion current with light, a phenomenon not seen for samples without PGSt.

[0041] The present inventors have identified novel and useful methods for the preparation of composite layers of a polymer of selected thiophenes, pyrroles, and anilines, and a redox polymer such as redox-active radical polymers. Such composite layers can be utilized as electrode-active material in a rechargeable battery, a (super)capacitor, or an organic solar cell. The composite layers can be also employed as electro-catalysts.

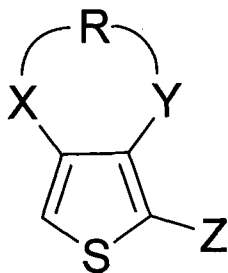
[0042] [Films cast from a solution]

Thus, one aspect of the present invention relates to a method for the preparation of a layer of a polymer of a monomer selected from the group consisting of thiophenes of the formula I wherein X and Y independently are selected from the group consisting of CH₂ and O, with the proviso that at least one of X and Y is -O-; R is optionally substituted C1-4-alkylene; Z is selected from hydrogen and amino; and R₁ and R₂ independently are selected from the group consisting of hydrogen, hydroxy, C1-6-alkyl, C1-6-alkoxy, C1-6-alkoxycarbonyl, C1-6-alkylcarbonyl, formyl, aryl, amino, mono and di(C1-6-alkyl)amino, carbamoyl, mono- and di(C1-6-alkyl)-amino-carbonyl, amino-C1-6-alkyl-aminocar-bonyl, mono and di(C1-6-alkyl)-amino-C1 6-alkyl-amino-carbonyl, C1-6-alkylcarbonyl-lami-no, cyano, carbamido, C1 6-alka-noyl-oxy, sulphonate (-SO₃H), C1-6-alkylsulphonyl-oxy, nitro, sulphonyl, dihalogen-C1-4-alkyl, trihalogen-C1-4-alkyl, and halogens; on a predetermined part of the surface of a substrate, said method comprising the steps of:

(a) providing a solution comprising the monomer, an Fe(III) salt, an amine/amide having a pK_a value of at least 1.0 selected from tertiary amines, tertiary amides and aromatic amines, and a solvent, wherein the molar ratio of the amine/amide to the Fe(III) salt is in the range of 0.35-1.25;

(b) applying the solution to the predetermined part of the surface of the substrate; and

(c) allowing the monomer to polymerize.



(I)

[0043] [Monomers]

The monomers, i.e. the thiophenes, are as defined hereinabove. X and Y are independently selected from the group consisting of CH₂ and O, with the proviso that at least one of X and Y is -O-; X and Y are preferably both -O-.

[0044] The biradical R is optionally substituted C1-4-alkylene. If substituted, the biradical R typically carries 1-3, such as 1-2, substituents. Illustrative examples of substituents which may be present are hydroxy, C1-6-alkyl, C1-6-alkoxy, C1-6-alkoxycarbonyl, C1-6-alkylcarbonyl, formyl, aryl, amino, mono and di(C1-6-alkyl)amino, carbamoyl, mono- and di(C1-6-alkyl)-amino-carbonyl, amino-C1-6-alkyl-aminocar-bonyl, mono and di(C1-6-alkyl)-amino-C1 6-alkyl-amino-carbonyl, C1-6-alkylcarbony-lami-no, cyano, carbamido, C1 6-alka-noyl-oxy, sulphono (-SO₃H), C1 6-alkylsulphonyl-oxy, nitro, sulphanyl, dihalogen-C1-4-alkyl, trihalogen-C1-4-alkyl, and halogens. Preferred examples are hydroxy, C1-6-alkyl, C1-6-alkoxy, C1-6-alkoxy-carbonyl, C1-6-alkylcarbonyl, amino, mono and di(C1-6-alkyl)amino, and halogen.

[0045] The biradical R is preferably unsubstituted ethylene, i.e. the group X-R-Y forms an ethylenedioxy group.

[0046] Z is selected from hydrogen and amino. Preferably, Z is hydrogen. R₁ and R₂ independently are selected from the group consisting of hydrogen, hydroxy, C1-6-alkyl, C1-6-alkoxy, C1-6-alkoxycarbonyl, C1-6-alkylcarbonyl, formyl, aryl, amino, mono and di(C1-6-alkyl)amino, carbamoyl, mono- and di(C1-6-alkyl)-amino-carbonyl, amino-C1-6-alkyl-aminocar-bonyl, mono and di(C1-6-alkyl)-amino-C1 6-alkyl-amino-carbonyl, C1-6-alkylcarbony-lami-no, cyano, carbamido, C1 6-alka-noyl-oxy, sulphono (-SO₃H), C1-6-alkylsulphonyl-oxy, nitro, sulphanyl, dihalogen-C1-4-alkyl, trihalogen-C1-4-alkyl, and halogens. Preferably R₁

and R2 are both hydrogen.

[0047] In view of the details given above, the monomer is preferably selected from the group consisting of 3,4-ethylenedioxythiophene (EDT), 2-amino-3,4-ethylenedioxythiophene, and, in particular the monomer is 3,4-ethylenedioxythiophene. Thiophene oligomers such as bithiophene and terthiophene with various substituents are also selected. The description in paragraphs [0019]-[0041] also shows examples of the present invention with reference to 3,4-ethylenedioxythiophene although other monomers are also believed to be useful.

[0048] [Amines/amides]

In the present description and claims, the terms “amines/amides” and “amine/amide” are intended to mean “amines or amides” and “amine or amide”, respectively.

[0049] In a particularly interesting embodiment, the term should have the meaning “amine”, thus referring to tertiary amines and aromatic amines (see below).

[0050] The amine to be used in the stabilized solution and methods of the invention should be an amine or amide (i.e. amine/amide) having a pKa value of at least 1.0 selected from tertiary amines, tertiary amide and aromatic amines. Thus in one embodiment, the amine/amide (here amine) is selected from tertiary amines, in particular selected from the group consisting of cyclic tertiary amines (such as 4-methylmorpholine, 1-methylpiperidine, 1-methylpyrrolidine); in another embodiment, the amine/amide (here amide) is selected from tertiary amide, in particular cyclic tertiary amides (such as N-methylpyrrolidone, N-vinylpyrrolidone and 3-methyl-2-oxazolidinone); and in still another embodiment, the amine/amide (here amine) is selected from aromatic amines, in particular selected from the group consisting of pyridine, N-methylimidazole, quinoline and isoquinoline. In a particularly interesting embodiment, the amine is selected from the group consisting of pyridine and derivatives of pyridine. A mixture of amines and/or amides may of course also be used.

[0051] It is believed to be highly advantageous to select the aromatic amines among those that do not contain an N-H group, e.g. aromatic amines should either contain an -N= group or an -NR- group.

[0052] A general requirement to the amine/amide is its pKa value which must be at least 1.0, in particular the amine/amide has a pKa value of at least 2.0, such as in the

range of 2.0-10.0, such as in the range of 3.5-7.0.

[0053] It is furthermore preferred, with regard to the ability of the amine/amide to evaporate after application of the solution to the predetermined part of the surface of the substrate, that the amine has a boiling point at 101.3 kPa of in the range of 50-210°C, such as in the range of 100-190°C.

[0054] [Chemical Oxidants]

The Fe(III) salt is typically one where the corresponding acid of the salt has a pKa value below 2.0. Illustrative examples of suitable Fe(III) salts are those selected from Fe(III) sulfonates and Fe(III) phosphates, in particular the Fe(III) tosylate salt. A mixture of Fe(III) salts may of course also be used.

[0055] A further important feature of the invention is that the molar ratio of the amine/amide to the Fe(III) salt is in the range of 0.35-1.25, in particular in the range of 0.4-1.0.

[0056] Although less critical, it is also preferred that the molar ratio between the monomer and the Fe(III) salt is in the range of 1:1.5 to 1:3.0, such as in the range of 1:2.0 to 1:2.5.

[0057] As alternatives to Fe(III) salts, nitrosonium hexafluorophosphate (NOPF6) and nitrosonium tetrafluoroborate (NOBF4) are also employed for VPP.

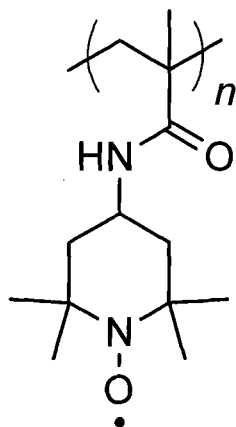
[0058] [Solvent]

The solvent is a crucial constituent for the methods of the invention, but is added in order to obtain a suitable viscosity of the solution. Co-solvents were carefully selected to ensure the solubility of both oxidants and redox polymers. Illustrative examples of suitable solvents are those selected from alcohols, water, ethers, acetates, glycols, glycerol and carboxylic acids, in particular the alcohols such as ethanol. A mixture of solvents may of course also be used.

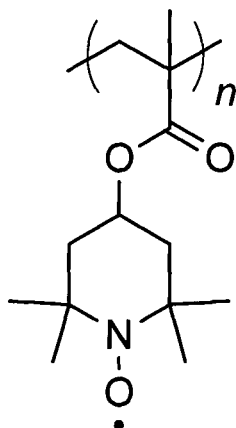
[0059] [Redox Polymers]

The redox polymers utilized in this invention are radical polymers, which are defined here as functional polymers densely substituted with redox-active side group. Redox-active radical groups are 2,2,6,6-tetramethylpiperidiny1-N-oxy (TEMPO), 2,2,5,5-tetramethylpyrrolidiny1-N-oxyl (PROXYL), nitronylnitroxide, galvinoxyl, phenylnitroxide, diphenylnitroxide, verdazyl. The backbone structures of the polymers are poly(methacrylate), poly(acrylate), poly(acrylamide), poly(vinyl ether), poly(ether),

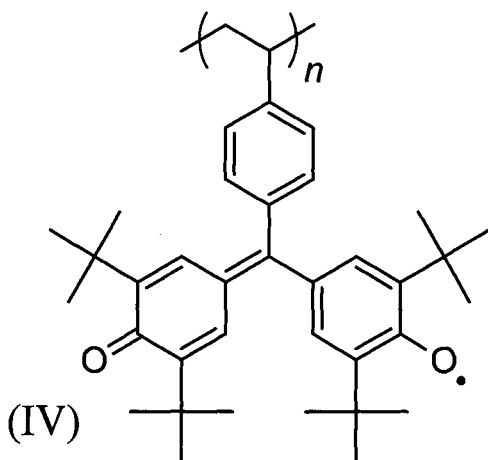
poly(norbornene), poly(styrene), poly(urethane), poly(urea), poly(ester), poly(amide), poly(imide), poly(phenyl ether), poly(phenyl sulfide). Some examples of radical polymers preferred in this invention are shown as formula II-VI. Other redox-active polymers such as poly(viologen) can be also applied.



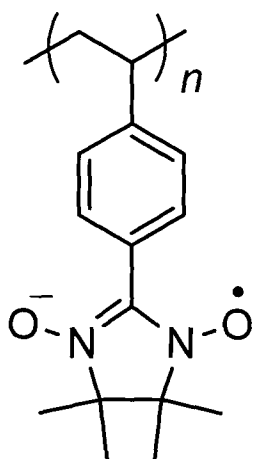
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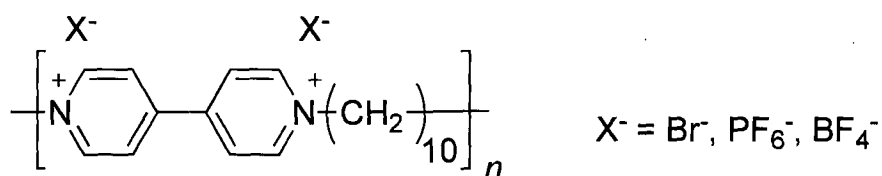
(III)



(IV)



(V)



(VI)

[0060] [Substrate]

A wide range of substrates are suitable in the methods of the invention, thus typically the solid substrate essentially consists of a material selected from polymers, e.g. polyolefins such as polyethylene (PE) and polypropylene (PP), and polystyrene (PS), and other thermoplastics such as fluoro-polymers (e.g. polytetrafluoroethylene (PTFE), tetrafluoroethylene-hexafluoropropylene copolymers (FEP), and polyvinylidene difluoride (PVDF)), polyamides (e.g. nylon 6 and nylon-11), polyvinylchloride (PVC), and rubbers; organosiloxane-based materials (e.g. silicone rubbers); glasses; silicon; paper; carbon fibres; ceramics; metals; etc.

[0061] It is often advantageous to prepare a predetermined pattern of the polymer layer, thus, the solution is preferably only applied to this predetermined part of the surface of the substrate. The pattern can be obtained by masking, by ink-jet printing, by imprint, by offset printing or by silk screen printing.

[0062] The substrate may be part of an object, or the substrate as such may constitute an object. Examples of very interesting objects for which the present invention is particularly applicable are micro-flow systems, "Lab on a chip", flat screens, solar cells, membranes, fabrics, clothes, and woven and non-woven fiber

materials.

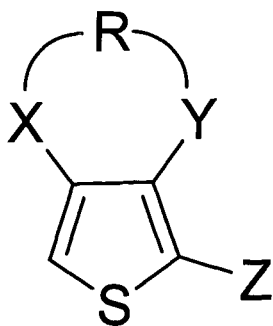
[0063] [Vapor phase polymerization of films]

Another aspect of the invention relates to a method for the preparation of a layer of a polymer of a monomer selected from the group consisting of thiophenes of the formula I, wherein X and Y independently are selected from the group consisting of CH₂ and O, with the proviso that at least one of X and Y is -O-; R is optionally substituted C1-4-alkylene; Z is selected from hydrogen and amino; and R1 and R2 independently are selected from the group consisting of hydrogen, hydroxy, C1-6-alkyl, C1-6-alkoxy, C1-6-alkoxycarbonyl, C1-6-alkylcarbonyl, formyl, aryl, amino, mono and di(C1-6-alkyl)amino, carbamoyl, mono- and di(C1-6-alkyl)-amino-carbonyl, amino-C1-6-alkyl-aminocar-bonyl, mono and di(C1-6-alkyl)-amino-C1-6-alkyl-amino-carbonyl, C1-6-alkylcarbonyl-lami-no, cyano, carbamido, C1-6-alka-noyl-oxy, sulphono (-SO₃H), C1-6-alkylsulphonyl-oxy, nitro, sulphonyl, dihalogen-C1-4-alkyl, trihalogen-C1-4-alkyl, and halogens; on a predetermined part of the surface of a substrate, said method comprising the steps of:

(a) providing a solution comprising an Fe(III) salt, an amine/amide having a pK_a value of at least 1.0 selected from tertiary amines, tertiary amines and aromatic amines, and a solvent, wherein the molar ratio of the amine/amide to the Fe(III) salt is in the range of 0.35-1.25; A redox polymer solution is added to prepare the mixed solution. Care should be taken in this preparation step, because the either Fe(III) salt or redox polymer precipitate out from the solution;

(b) applying the solution to the predetermined part of the surface of the substrate so as to form a film on said predetermined part of the surface of the substrate;

(c) exposing said film to a vapor comprising the monomer, and allowing said monomer to polymerize.



(I)

[0064] As it will be realized, the specifications and preferences with respect to the monomer(s), the amine(s)/amide(s), the Fe(III) salt, the solvent and the substrate is as described above for “Films cast from a solution”. Furthermore, the method may – as above – comprise the additional step (d) of washing the polymer film so as to remove the Fe(II)/Fe(III) salt and any remaining amine.

[0065] [Step (a)]

The first step (a) of the method is to provide a solution comprising an Fe(III) salt, an amine/amide having a pKa value of at least 1.0 selected from tertiary amines, tertiary amides and aromatic amines, and a solvent, wherein the molar ratio of the amine/amide to the Fe(III) salt is in the range of 0.35-1.25. This is typically done by simple mixing of the constituents. It should be noted that the solution does typically not include a monomer, although a minor amount of monomer may be present, if desirable.

[0066] [Step (b)]

In a subsequent step (b), the solution is applied to the predetermined part of the surface of the substrate so as to form a film on said predetermined part of the surface of the substrate. The solution is typically applied by spraying, dipping, printing or spin coating. During and after the drying of the Fe(III) salt/(amine/amide) mixture it is advantageous to raise the temperature to 40-70°C. This helps to avoid formation of large crystals in the film.

[0067] [Step (c)]

In a final step (c), the film is exposed to a vapor comprising the monomer, and the monomer is allowed to polymerize. During the polymerization, which may last for more than one hour, it is advantageous to raise the temperature in the polymerization chamber (Figure 1) to 40-150°C, such as 40-90°C or 40-80°C and float the chamber with a selected gas. This facilitates evaporation of the amine/amide and speeds up the polymerization.

[0068] [Step (d)]

The method may comprise the additional step (d) of washing the polymer film so as to remove the Fe(II)/Fe(III) salt and any remaining amine/amide. The reduced Fe(II) salt and excess of amine/amide and Fe(III) salt has not positive effect on the conducting polymer and is therefore unwanted in the final product. These unwanted

products are easily removed by washing the conducting polymer once or twice with water or ethanol.

[0069] [Addition of a polymer or polymer precursor]

In one embodiment, the solution in step (a) further comprises a polymer or a polymer precursor. Examples of such polymer precursors are curable glues, such as heat or UV-curable glues. This embodiment appears to be particularly relevant for this aspect of the invention.

[0070] [Base-inhibited oxidative polymerization]

Monomer can be mixed to the oxidant solution prior to the spin-coating. In this case, amines need to be added as inhibitor.

[0071] [Step (a)]

The first step (a) of the method is to provide a solution comprising the monomer, an Fe(III) salt, an amine/amide having a pKa value of at least 1.0 selected from tertiary amines, tertiary amides and aromatic amines (in particular tertiary amines and aromatic amides), and a solvent, wherein the molar ratio of the amine/amide to the Fe(III) salt is in the range of 0.35-1.25. A redox polymer solution is added to prepare the mixed solution. Care should be taken in this preparation step, because the either Fe(III) salt or redox polymer precipitate out from the solution. the amine/amide have to be mixed in the solvent before the monomer is added, and the temperature should preferably be kept at 25°C or lower.

[0072] [Step (b)]

In a subsequent step (b), the solution is applied to the predetermined part of the surface of the substrate. The solution is typically applied by spraying, dipping, printing or spin coating.

[0073] [Step (c)]

In a final step (c), the substrate is installed into the chamber with monomer vapor, and the monomer is allowed to polymerize. The polymerization process can be promoted by elevating the temperature to 40-150°C, such as 40-90°C, and/or by applying reduced pressure in order to remove the solvent and the amine/amide.

[0074] [Step (d)]

The method may comprise the additional step (d) of washing the polymer film so as to remove the Fe(II)/Fe(III) salt and any remaining amine/amide. The reduced

Fe(II) salt and excess of amine/amide and Fe(III) salt has no positive effect on the conducting polymer and is therefore unwanted in the conductive layer. These unwanted products are easily removed by washing the conducting polymer once or twice with water or ethanol.

[0075] [Addition of a polymer or polymer precursor]

In one embodiment, the solution in step (a) further comprises a polymer or a polymer precursor which provides advantages with respect to the pre/post-functionalization. Examples of such polymer precursors are curable glues, such as heat or UV-curable glues.

[0076] [Further aspects of the invention]

In view of the first of the above-mentioned aspects, it has also been found that the stabilized solution prepared in step (a) constitutes a particularly interesting aspect of the invention.

[0077] Thus, the invention also provides a stabilized solution of a polymerizable solution comprising a monomer selected from thiophenes of the formula I and anilines of the formula II and an Fe(III) salt in a solvent, said solution further comprising an amine/amide having a pKa value of at least 1.0 selected from tertiary amines, tertiary amides and aromatic amines, wherein the molar ratio of the amine/amide to the Fe(III) salt is in the range of 0.35-1.25.

[0078] It has also proven possible to obtain substrates with a layer of an electrically conducting polymer layer with an unprecedented conductivity.

[0079] Thus, the present invention also provides a substrate comprising a layer of poly(3,4-ethylenedioxythiophene) on at least a part of the surface thereof, said layer having a conductivity of at least 700 S/cm. The layer is preferably prepared according to one of the methods defined herein.

[0080] [Preferred embodiment]

In a currently most preferred embodiment of the aspects of the invention, the monomer is 3,4-ethylenedioxythiophene (EDT), the Fe(III) salt is Fe(III) tosylate, and the amine/amide is pyridine.

[0081] The obtained conducting polymer/redox polymer composite was utilized as electrode-active material to fabricate a secondary battery. The composition was modified with the feed ratio of the oxidizing agent and redox polymer, to be 10 – 80

wt% for the radical polymer content in the composite. A coin or laminate cell was fabricated with the obtained composite cathode and lithium or carbon anode with separator film and lithium-based electrolyte solution. When utilizing with PEDOT/PTAm cathode, the cell exhibited 3.6 V and 500 cycles. The charge capacity was 100 – 120 mAh/g. Alternative to the lithium/carbon anodes, n-type radical polymers such as PGSt were utilized as anode, and the cell exhibited 0.5 – 1.5 V, corresponded to the redox potential gap between p- and n-type redox polymers.

[0082] The obtained composite can be also utilized for electrocatalyst. Combined with redox molecules, the overpotential for PEDOT-catalyzed electro-reduction of oxygen can be lowered. The composite can be also used as SO₂ degradation.

[0083] The doping level of PEDOT prepared by this method is generally 20–30%, but chemical dedoping with reducing agents such as hydrazine affords the corresponding electrically neutral polymer. Doping level of the polymer can be confirmed by the color and UV-vis spectral change. Dedoped polythiophene derivatives exhibited fluorescence at 450 – 650 nm. In presence of electron acceptors such as fullerene, viologen, or imide derivatives, in-situ oxidative polymerization and the following dedoping yields electron donor/acceptor mixed layer for photo-conversion in organic photovoltaics.

[0084] Metal-free (iron-free) oxidizing agents such as nitrosonium hexafluorophosphate (NOPF₆) and nitroxonium tetrafluoroborate (NOBF₄) were also employed for VPP. Oxidizing agents above can be employed as vapor, thus thiophene monomers are not necessary to be supplied as vapor. Thiophene derivatives having low vapor pressure, such as terthiophene and thienothiophene were applicable. As the step (a), terthiophene was dissolved in chloroform (10 mg/mL) and the solution was coated on the aforementioned substrate. The substrate was set in the chamber containing 10 wt% acetonitrile solution of NOPF₆. After 1 h, the polythiophene was formed on the substrate, washed with isopropyl alcohol to give light reddish brown color of polythiophene film.

[0085] The obtained film was dedoped by treatment with hydrazine vapor to give the dedoped polythiophene film. The film was examined as donor material for photo-current conversion.

[0086] It is to be understood that the above-described embodiments are illustrative

of only a few of the many possible specific embodiments which can represent applications of the principles of the invention. Numerous and varied other arrangements can be readily devised by those skilled in the art without departing from the spirit and scope of the invention.

Claims

1. A method for preparing a conductive composition containing organic redox molecules and a conducting polymer, the method comprising the steps of ;
 - (a) preparing a composition containing the organic redox molecules and an oxidant,
 - (b) adding an aromatic derivative to the composition and forming the conductive polymer through an oxidative polymerization of the aromatic derivative, and
 - (c) removing at least part of the oxidant from the composition treated by the step (b).
2. The method of claim 1, wherein the oxidative polymerization is a vapor-phase oxidative polymerization.
3. The method of claim 2, wherein the vapor-phase oxidative polymerization is carried out in presence of the organic redox molecules.
4. A method of claim 1, wherein the conductive composition further contains a non-conductive polymer selected from the group consisting of poly-glycols, polyvinyl-alcohols, polysaccharides, and a mixture thereof, and

Wherein, in the step (a), the composition is prepared to further contain the non-conductive polymer.
5. The method of claim 1, wherein the organic redox molecules are selected from a group consisting of organic stable radical compound, viologen, fullerene derivative, their precursors, and a mixture thereof.

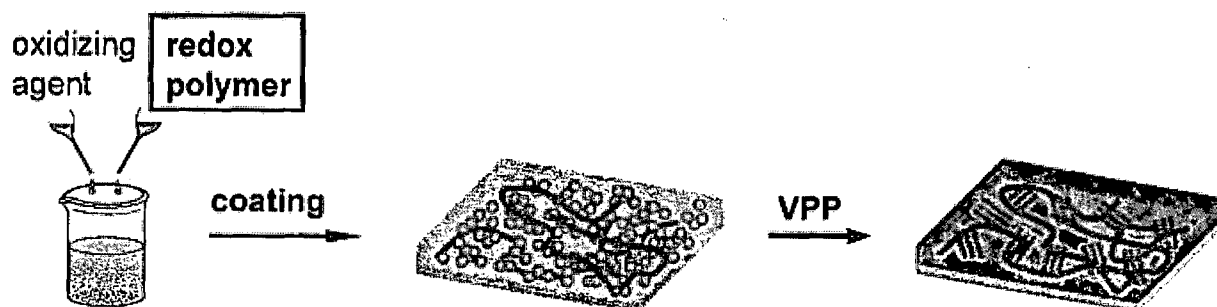
6. The method of claim 1, wherein the organic redox molecules are characterized as a non-conducting polymer bearing robust but redox-active organic groups such as nitroxide, galvinoxyl, and nitronyl nitroxide.
7. The method of claim 1, wherein the organic redox molecules are characterized as a non-conducting polymer bearing redox-active group such as viologen or quinone.
8. The method of claim 1, wherein the composition is formed by the steps of providing a solution containing the organic redox molecules, the oxidant and a solvent, and drying the solution.
9. The method of claim 1, wherein the conducting polymer is defined by polymer substance of heteroaromatic congeners.
10. The method of claim 1, wherein the aromatic derivative is 3,4-Ethylenedioxythiophene.
11. The method of claim 1, wherein the oxidant is selected from $\text{Fe}(\text{OTs})_3$.
12. A rechargeable battery comprising the conductive composition of claim 1 as an electrode active material.
13. An organic photoelectric conversion element comprising the conductive composition of claim 1 as an active layer.
14. An electro catalyst used for oxygen reduction, water-splitting reaction, decomposition of sulfur dioxide, and oxidation reaction for fuel-cells comprising the conductive composition of claim 1.
15. An electrode comprising
a conducting composition containing the organic redox molecules, the conducting polymer, and a dopant,

wherein the dopant is selected from the group consisting of p-toluenesulfonate anion (OTs⁻), hexafluorophosphate anion (PF₆⁻), tetrafluoroborate anion (BF₄⁻), and a mixture thereof.

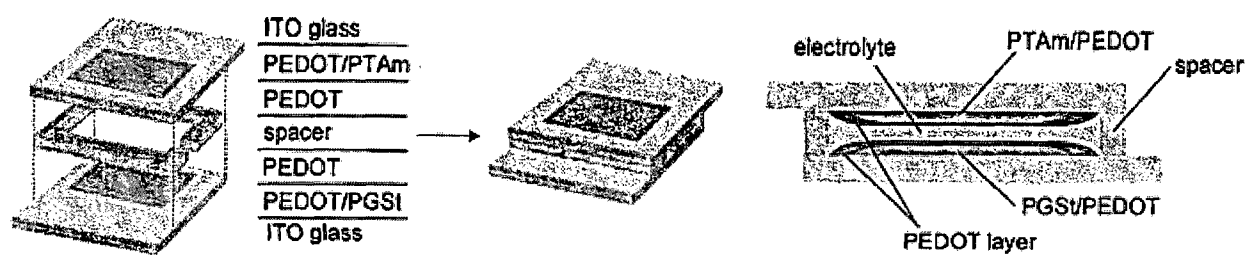
16. The electrode of claim 14, wherein the conducting composition has an electric conductivity higher than 1 S/cm when it is measured by four-terminal method.

17. An organic photoelectric conversion element comprising the conductive composition of claim 1 as an active layer.

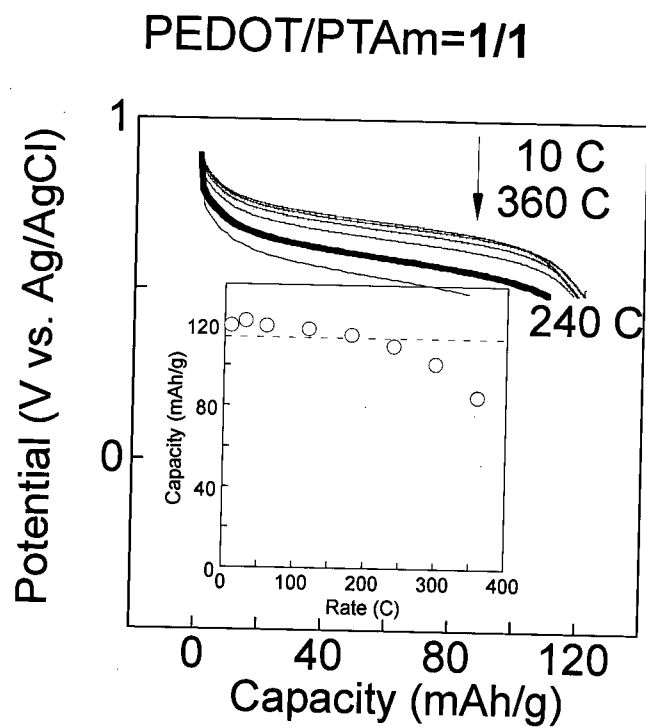
[Fig. 1]



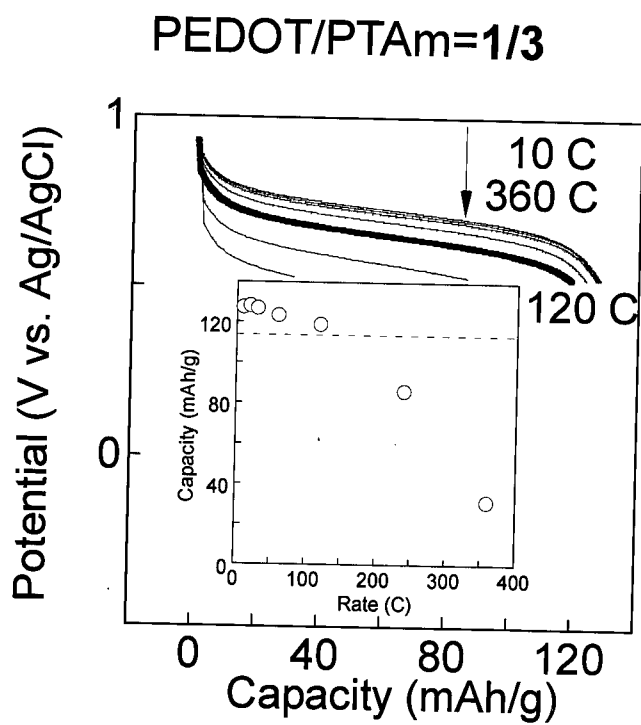
[Fig. 2]



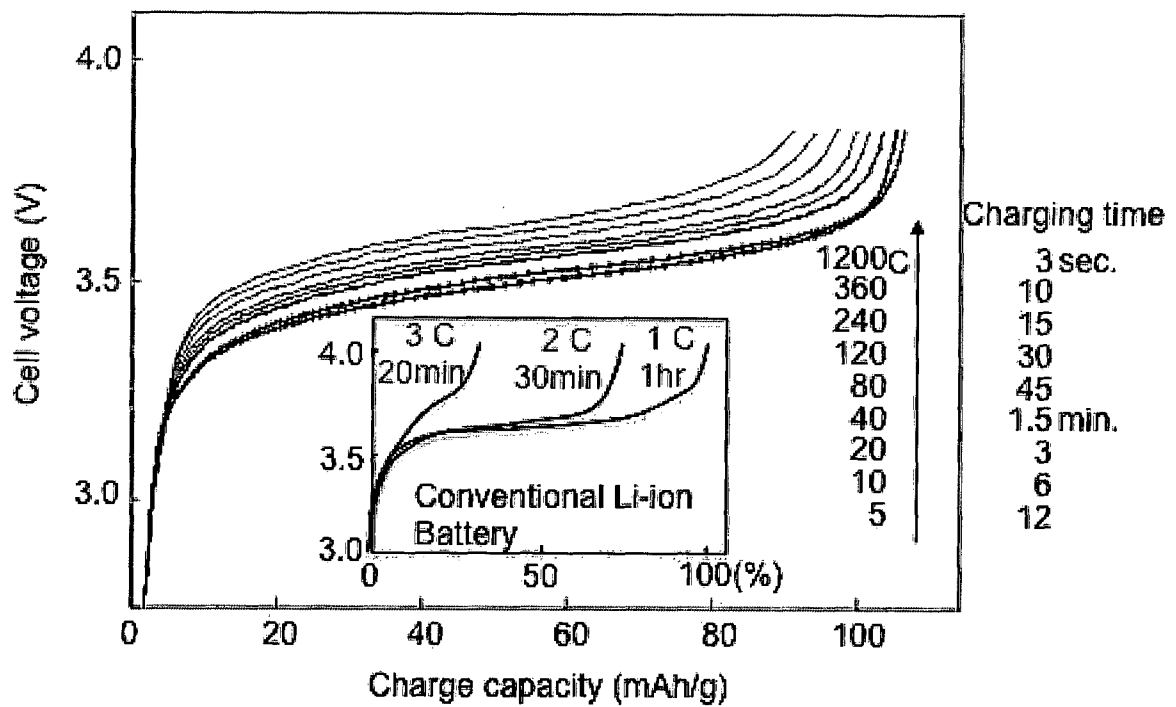
[Fig. 3]



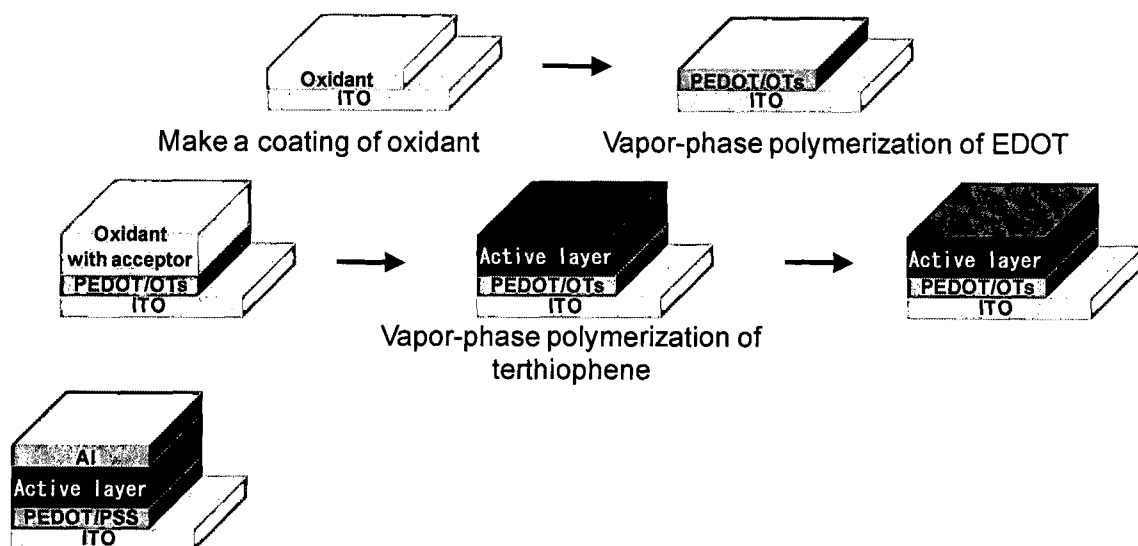
[Fig. 4]



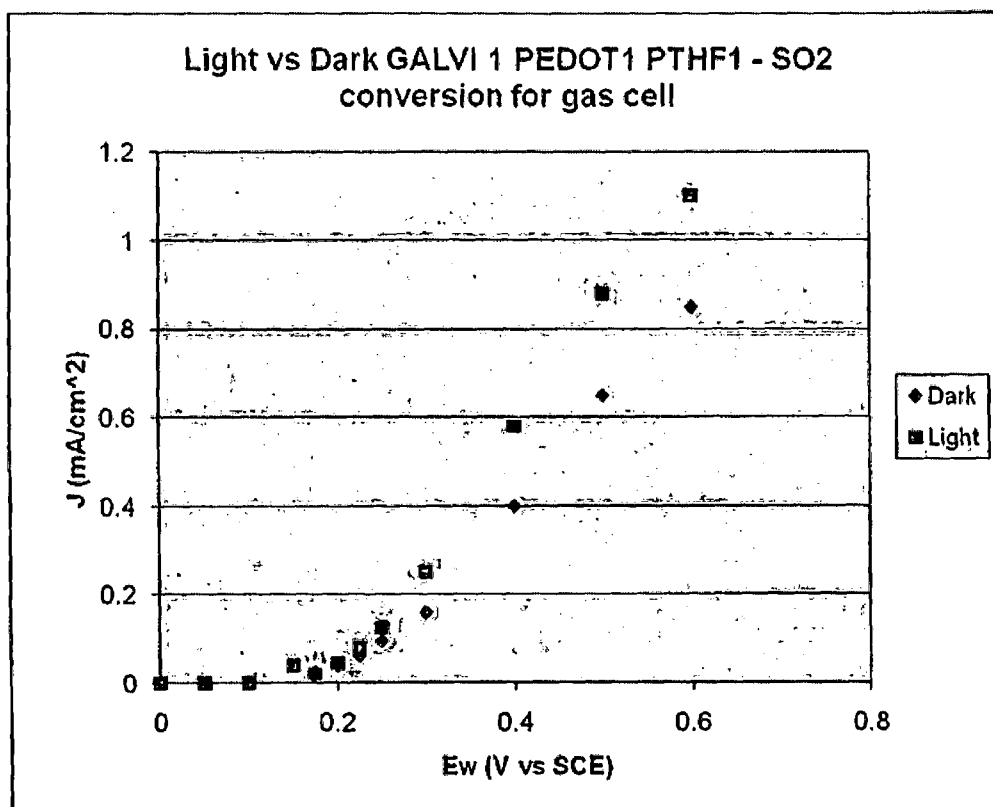
[Fig. 5]



[Fig. 6]



[Fig. 7]



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2012/056782

A. CLASSIFICATION OF SUBJECT MATTER

Int.Cl. C08L65/00 (2006.01) i, C08L101/12 (2006.01) i, H01B1/12 (2006.01) i,
H01B13/00 (2006.01) i, H01L51/42 (2006.01) i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Int.Cl. C08L65/00, C08L101/12, H01B1/12, H01B13/00, H01L51/42

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

Published examined utility model applications of Japan 1922-1996
Published unexamined utility model applications of Japan 1971-2012
Registered utility model specifications of Japan 1996-2012
Published registered utility model applications of Japan 1994-2012

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

JSTPlus/JMEDPlus/JST/580 (JDreamII)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y A	JP 61-502261 A (BATTELLE-INSTITUT) 1986.10.09, Claims & EP 185063 A1 & WO 1985/005728 A1 & DE 3419788 A & DE 3419788 A1 & CA 1269194 A	1, 4, 5, 8-17 10, 11 2, 3, 6, 7
Y A	JP 2010-143980 A (TOYO INK MFG CO LTD) 2010.07.01, Claims, Examples (No Family)	10, 11 1-9, 12-17
A	JP 2008-156636 A (CAMBRIDGE DISPLAY TECHNOLOGY LTD) 2008.07.10, Claims, 【0037】 & US 6777706 B1 & US 2004/0220332 A1 & GB 9815271 A & EP 1432051 A2 & EP 1995800 A2 & WO 2000/004593 A1 & WO 2000/060612 A1 & DE 60012000 D & DE 60012000 T & AU 3977900 A & AT 270788 T & KR 10-2006-0114035 A & CN 1316105 A & CN 1349651 A & HK 1038638 A	1-17

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:

“A” document defining the general state of the art which is not considered to be of particular relevance

“E” earlier application or patent but published on or after the international filing date

“L” document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

“O” document referring to an oral disclosure, use, exhibition or other means

“P” document published prior to the international filing date but later than the priority date claimed

“T” later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

“X” document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

“Y” document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

“&” document member of the same patent family

Date of the actual completion of the international search

13.06.2012

Date of mailing of the international search report

26.06.2012

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2012/056782

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2010/051259 A1 (PLEXTRONICS INC) 2010.05.06, Claims, Examples & US 2010/0108954 A1 & EP 2350166 A & WO 2010/051259 A1 & KR 10-2011-0079679 A & JP 2012-506923 A	1-17
A	JP 2007-070384 A (UNIV WASEDA GH) 2007.03.22, Whole document (No Family)	1-17
A	Macromolecules, 2007, 40, 3167-73	1-17
A	J. Electrochem. Soc., 1996, 143, 2310-4	1-17
P, X	The Chemical Society of Japan, Proceedings, 91 (3), 2011.03, 890, 1 E1-32	1-17

(1) "Organic redox molecules" in claims 1-5, 8-17 are quite broad concept and a huge number of compounds correspond to it.

In the description, however, only several types of "Redox polymer" are disclosed (See [0020]-[0041], [0059]).

Therefore, claims 1-5, 8-17 are not supported by the description as required by Article 6 PCT as their scope is broader than justified by the description and drawings.

(2) Claim 4 is not sufficiently supported by the description.

In the description, the conductive composition "further" contains a non-conductive polymer is not disclosed.

(3) The definition of "organic redox molecules" is ambiguous.

While claim 5 teaches "the organic redox molecules are selected from a group consisting of ... fullerene derivative, their precursors, and a mixture thereof.", "fullerene" is not "organic" molecule.