

DESCRIPTION

TITLE OF THE INVENTION: CONDUCTIVE COMPOSITION AND METHOD FOR PRODUCING CONDUCTIVE COATING FILM

TECHNICAL FIELD

[0001]

The present invention relates to conductive compositions. Particularly, the present invention relates to an conductive composition comprising a conductive polymer and a dopant having a specific chemical structure; an electrode produced by using the conductive composition for a solid electrolyte capacitor; a solid electrolyte capacitor produced by using the conductive composition; and a method for producing a conductive coating film formed from the conductive composition.

BACKGROUND ART

[0002]

In recent years, development of conductive polymeric compounds capable of imparting electroconductivity at low temperature onto flexible substrates has been attempted, and such compounds are expected to be applied to conductive functional materials, light-emissive functional materials, optoelectronic conversion functional materials, and so on.

[0003]

Heretofore, it is known that compounds having a sulfonic

acid group as a dopant are suitable as conductive polymers capable of affording conductive coating films (see, for example, Patent Documents 1 and 2).

[0004]

In Patent Document 1 has been proposed a coating liquid in the form of an aqueous colloidal dispersion using polystyrene sulfonic acid as a dopant. However, this coating liquid has so high hydrophilicity that a conductive coating film produced by using this coating liquid is highly hygroscopic and there are problems such as that highly acidic hydrogen ions generated from the absorbed moisture will corrode metal which is in contact with the coating liquid. Moreover, the conductive coating film formed from the coating liquid has an electroconductivity of about 100 S/cm, which is not sufficient conductivity required in use for conductive functional materials.

[0005]

In Patent Document 2 has been proposed a method of using a polycondensed compound having a sulfonic acid group as a dopant, and a film that exhibits good electroconductivity has been obtained by performing electrolytic oxidation polymerization. However, the conductive coating film formed from the coating liquid has an electroconductivity of about 100 S/cm, which is not sufficient conductivity required in use for conductive functional materials.

PRIOR ART DOCUMENTS

PATENT DOCUMENTS

[0006]

Patent Document 1: JP-A-7-90060

Patent Document 2: JP-A-2007-224182

DISCLOSURE OF THE INVENTION

PROBLEMS TO BE SOLVED BY THE INVENTION

[0007]

An object of the present invention is to provide a conductive composition which can form a conductive coating film with less corrosiveness and high electroconductivity.

SOLUTIONS TO THE PROBLEMS

[0008]

The present invention is a conductive composition (A) comprising a sulfur trioxide complex and a substituted polythiophene (P) having thiophene repeating units at least some of which are each a thiophene repeating unit (α) substituted at the 3-position and/or the 4-position of its thiophene ring with at least one group selected from the group consisting of

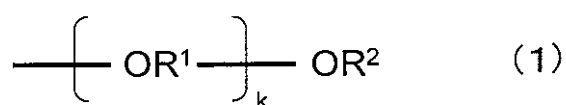
(a) a polyether group represented by general formula (1) given below,

(b) an alkoxy group having 1 to 15 carbon atoms,

(c) an alkoxyalkyl group having 2 to 19 carbon atoms, and
 (d) an alkyl group having 1 to 15 carbon atoms or an alkyl group of which a hydrogen atom has been substituted with the polyether group (a).

[0009]

[Chem. 1]



[0010]

In the formula, OR¹ represents an oxyalkylene group having 2 to 4 carbon atoms, R² represents an alkyl group having 1 to 15 carbon atoms, and k is an integer of 1 to 9.

ADVANTAGES OF THE INVENTION

[0011]

The conductive composition of the present invention are so lowly corrosive that it can be applied to metal or the like which are prone to be corroded and the conductive coating film has high electroconductivity, it can be expected to be applied to various conductive functional materials.

MODE FOR CARRYING OUT THE INVENTION

[0012]

The conductive composition (A) of the present invention comprises a substituted polythiophene (P) and a sulfur trioxide

complex as a dopant, the substituted polythiophene (P) having thiophene repeating units at least some of which are each a thiophene repeating unit (α) substituted at the 3-position and/or the 4-position of its thiophene ring with at least one group selected from the group consisting of a polyether group (a) defined above, an alkoxy group (b) defined above, an alkoxyalkyl group (c) defined above, and an alkyl group (d) defined above (in this description, also referred to as a "thiophene repeating unit (α)").

[0013]

The aforementioned polyether group (a) is a polyether group represented by the general formula (1) and having repeating units each made up of an oxyalkylene group having 2 to 4 carbon atoms, the number of the repeating units being 1 to 9, and one terminal of the polyether group being an alkoxy group having 1 to 15 carbon atoms.

Examples of the oxyalkylene group having 2 to 4 carbon atoms include an oxyethylene group, an oxypropylene group, oxybutylene and the like.

[0014]

Examples of the terminal alkoxy group having 1 to 15 carbon atoms include a methoxy group, an ethoxy group, a propoxy group, an isopropoxy group, a n-, iso-, sec- or a tert-butoxy group, a pentyloxy group, a hexyloxy group, a heptyloxy group, an octyloxy group, a 2-ethylhexyloxy group, a nonyloxy group, a

decyloxy group, an undecyloxy group, a dodecyloxy group, a tridecyloxy group, a tetradecyloxy group, a pentadecyloxy group and the like.

[0015]

Examples of the alkoxy group (b) include alkoxy group having 1 to 15 carbon atoms which are the same as those provided as examples for the aforementioned polyether group (a).

[0016]

Examples of the aforementioned alkoxyalkyl group (c) include alkyl groups having 1 to 4 carbon atoms substituted with alkoxy groups having 1 to 15 carbon atoms. Examples of the alkoxy groups having 1 to 15 carbon atoms include alkoxy groups which are the same as those provided as examples for the aforementioned polyether group (a), and examples of the alkyl groups having 1 to 4 carbon atoms include a methyl group, an ethyl group, a n- or iso-propyl group, a n-, sec-, iso-, or tert-butyl group and the like.

[0017]

Examples of the alkyl group (d) that the thiophene repeating unit (α) has include a linear or branched alkyl group having 1 to 15 carbon atoms, e.g., a methyl group, a n- or iso-propyl group, a n-, iso-, sec- or tert-butyl group, a n- or iso-pentyl group, a cyclopentyl group, a n- or iso-hexyl group, a cyclohexyl group, a n- or iso-heptyl group, a n- or iso-octyl group, a 2-ethylhexyl group, a n- or iso-nonyl group,

a n- or iso-decyl group, a n- or iso-undecyl group, a n- or iso-dodecyl group, a n- or iso-tridecyl group, a n- or iso-tetradecyl group, and a n-, or iso-pentadecyl group.

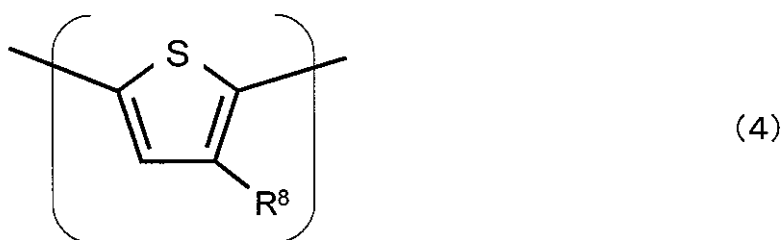
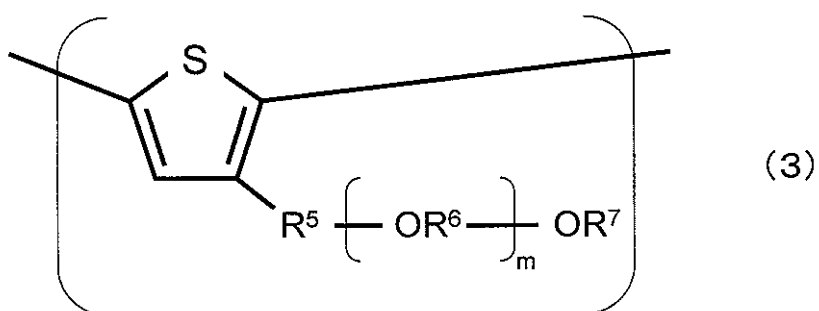
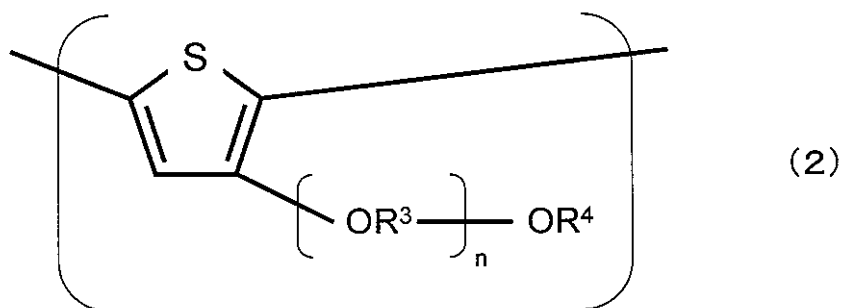
The alkyl group (d) may be an alkyl group resulting from the substitution of a hydrogen atom of the above-mentioned alkyl group with the aforementioned polyether group (a).

[0018]

One preferred from the viewpoint of electroconductivity as the thiophene repeating unit (α) that the substituted polythiophene (P) in the present invention has is a repeating unit ($\alpha 1$) represented by the following general formula (2), a repeating unit ($\alpha 2$) represented by the following general formula (3), or a repeating unit ($\alpha 3$) represented by the following general formula (4).

[0019]

[Chem. 2]



[0020]

OR³ in the above general formula (2) and OR⁶ in the above general formula (3) each independently represent an oxyethylene group or an oxypropylene group, and an oxyethylene group is preferred from the viewpoint of electroconductivity.

[0021]

R⁴, R⁷, and R⁸ in the above general formulae (2) through (4) each independently represent a linear or branched alkyl group having 1 to 12 carbon atoms (e.g., a methyl group, a n-

or iso-propyl group, a n-, iso-, sec- or tert-butyl group, a n- or iso-pentyl group, a cyclopentyl group, a n- or iso-hexyl group, a cyclohexyl group, a n- or iso-heptyl group, a n- or iso-octyl group, a 2-ethylhexyl group, a n- or iso-nonyl group, a n- or iso-decyl group, a n- or iso-undecyl group, and a n-, or iso-dodecyl group).

[0022]

When the below-described n is 1 or more, a group preferred as R^4 from the viewpoint of electroconductivity is a linear or branched alkyl group having 1 to 6 carbon atoms and more preferably a linear or branched alkyl group having 1 to 4 carbon atoms.

When n is 0, a group preferred as R^4 from the viewpoint of electroconductivity is a linear or branched alkyl group having 3 to 12 carbon atoms and more preferably a linear or branched alkyl group having 6 to 12 carbon atoms.

[0023]

When the below-described m is 1 or more, a group preferred as R^7 from the viewpoint of electroconductivity is a linear or branched alkyl group having 1 to 6 carbon atoms and more preferably a linear or branched alkyl group having 1 to 4 carbon atoms.

When m is 0, a group preferred as R^7 from the viewpoint of electroconductivity is a linear or branched alkyl group having 3 to 12 carbon atoms and more preferably a linear or

branched alkyl group having 6 to 12 carbon atoms.

[0024]

A group preferred as R^8 from the viewpoint of solvent solubility and electroconductivity is a linear or branched alkyl group having 3 to 12 carbon atoms and more preferably a linear or branched alkyl group having 6 to 12 carbon atoms.

[0025]

R^5 in the above formula (3) represents a linear or branched alkylene group having 1 to 4 carbon atoms (e.g., a methylene group, an ethylene group, a 1,2- or 1,3-propylene group, and a 1,2-, 1,3-, 2,3- or 1,4-butylene group), and groups preferred from the viewpoint of solvent solubility and electroconductivity are linear or branched alkylene groups having 1 to 3 carbon atoms, and more preferably a methylene group or an ethylene group.

[0026]

n and m in the above general formula (2) or (3) are each independently an integer of 0 to 5. From the viewpoint of solvent solubility and electroconductivity, n is preferably 1 to 5, more preferably 2 to 5. From the viewpoint of solvent solubility and electroconductivity, m is preferably 0 to 4, and m is more preferably 0 to 3.

[0027]

The substituted polythiophene (P) in the present invention may consist only of the above-described thiophene

repeating units (α) or alternatively may contain thiophene repeating units that are not substituted along with the repeating units (α).

[0028]

From the viewpoint of solvent solubility, the content of the above-described thiophene repeating units (α) in the substituted polythiophene (P) is preferably 50 to 100% by weight, more preferably 60 to 100% by weight, and particularly preferably 70 to 100% by weight based on the weight of the substituted polythiophene (P).

[0029]

The substituted polythiophene (P) in the present invention can be synthesized by a known method, such as anionic polymerization or oxidation polymerization of monomers corresponding to respective repeating units.

[0030]

Examples of a monomer corresponding to the above-described thiophene repeating unit (α) include thiophenes substituted with the polyether group (a) defined above, the alkoxy group (b) defined above, the alkoxyalkyl group (c) defined above or the alkyl group (d) defined above at the 3-position and/or the 4-position of its thiophene ring and also substituted with a halogen atom at the 2-position and the 5-position.

Thiophene is recited as a monomer corresponding to the

unsubstituted thiophene repeating unit.

[0031]

From the viewpoint of solubility, the content of the substituted polythiophene (P) in the conductive composition (A) is preferably 0.1 to 20% by weight, more preferably 1.0 to 6.0% by weight based on the weight of the conductive composition (A). It is undesirable that the content of the substituted polythiophene (P) is larger because an agglomerate generates, resulting in deterioration of applicability. It is undesirable that the content of the substituted polythiophene (P) is smaller because it becomes difficult to form a uniform conductive coating film.

[0032]

The regioregularity (RR) of the substituted polythiophene (P) in the present invention is usually 50% or more, and from the viewpoint of electroconductivity, it is more preferably 80% or more, even more preferably 90% or more.

[0033]

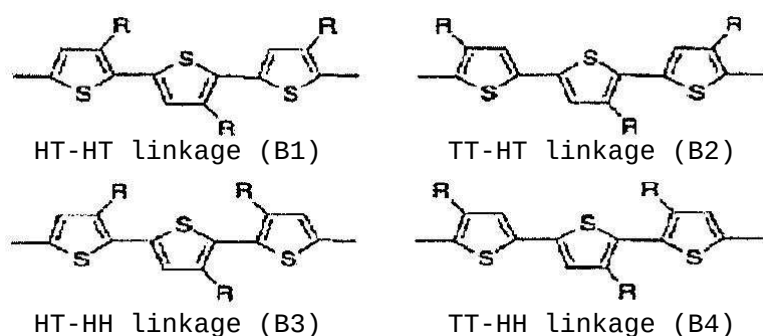
The definition of the regioregularity (RR) in the present invention is described below.

The bond of the substituted polythiophene (P) includes four types as illustrated in the following chemical formulae, i.e., a HT-HT linkage (B1), a TT-HT linkage (B-2), a HT-HH linkage (B3), and a TT-HH linkage (B4). As used herein, HT is an abbreviation of Head-to-Tail, TT is an abbreviation of

Tail-to-Tail, and HH is an abbreviation of Head-to-Head.

[0034]

[Chem. 3]



[0035]

R in the chemical formulae of the foregoing four linkage types each independently represents the polyether group (a) defined above, the alkoxy group (b) defined above, the alkoxyalkyl group (c) defined above, or the alkyl group (d) defined above.

[0036]

The regioregularity (RR) of the substituted polythiophene (P) in the present invention is defined by the ratio (%) of HT-HT linkages (B1) in the substituted polythiophene (P) and it is calculated by the following expression (1):

$$\text{Regioregularity (RR)} = B1 \times 100 / (B1 + B2 + B3 + B4) \quad (1)$$

B1 represents the number of HT-HT linkages, B2 represents the number of TT-HT linkages, B3 represents the number of HT-HH linkages, and B4 represents the number of TT-HH linkages.

[0037]

Specifically, since the protons in these linkages have each exhibit their unique chemical shifts (δ) in nuclear magnetic resonance spectrometry (^1H -NMR), it can be calculated from the integrals of the peaks at the chemical shifts corresponding to the four types of linkages.

In the case of polythiophene derivative having a repeating unit ($\alpha 3$) represented by general formula (3), HT-HT linkage (B1): $\delta = 6.98$, TT-HT linkage (B2): $\delta = 7.00$, HT-HH linkage (B3): $\delta = 7.02$, and TT-HH linkage (B4): $\delta = 7.05$ are specifically exhibited. Therefore, integrals S1, S2, S3, and S4 of the peaks at the chemical shifts peculiar to (B1), (B2), (B3), and (B4) are calculated, and then a regioregularity (RR) is calculated by the following formula (2) using the ratio (%) of the integral S1 of the peak at the chemical shift peculiar to (B1) relative to the sum total of those integrals.

$$\text{Regioregularity (RR)} = S1 \times 100 / (S1 + S2 + S3 + S4) \quad (2)$$

The measurement of the ^1H -NMR was carried out by using a measurement instrument: AVANCE III400 digital NMR [manufactured by Bruker BioSpin K.K.] under conditions including a measurement solvent: deuterated chloroform and a measurement temperature: 27°C.

[0038]

The substituted polythiophene (P), which is a conductive polymer, donates an electron to a sulfur trioxide complex as

a dopant to form a charge transfer complex together with the dopant. Since such a charge transfer complex develops electroconductivity as a carrier of electrons, higher concentrations of the sulfur trioxide complex are preferred. However, if the concentration is excessively high, the electroconductivity will deteriorate. Therefore, the used amount of the sulfur trioxide complex is preferably 5 to 300% by weight, more preferably 10 to 150% by weight relative to the substituted polythiophene (P).

[0039]

A sulfur trioxide complex is a complex of sulfur trioxide with a Lewis base such as ethers, amides, amines, and sulfides. Examples of ether-sulfur trioxide complexes include sulfur trioxide-dioxane complexes, sulfur trioxide-dioxolane complexes, sulfur trioxide-dimethyl ether complexes, sulfur trioxide-ethyl methyl ether complexes, and sulfur trioxide-diethyl ether complexes; examples of amide-sulfur trioxide complexes include sulfur trioxide-N,N-dimethylformamide complexes, and so on; examples of amine-sulfur trioxide complexes include sulfur trioxide-pyridine complexes, sulfur trioxide-triethylamine complexes, sulfur trioxide-trimethylamine complexes, and sulfur trioxide-N-ethyldiisopropylamine complexes; and examples of sulfide-sulfur trioxide complexes include sulfur trioxide-dimethylsulfide complexes, sulfur

trioxide-ethylmethylsulfide complexes, and sulfur trioxide-diethylsulfide complexes. Out of these, the amide-sulfur trioxide complexes and the amine-sulfur trioxide complexes are preferable in terms of electroconductivity, and sulfur trioxide-N,N-dimethylformamide complexes are more preferable among the amide-sulfur trioxide complexes and sulfur trioxide-pyridine complexes are more preferable among the amine-sulfur trioxide complexes.

[0040]

The conductive composition (A) of the present invention comprises a sulfur trioxide complex as a dopant and can further comprise other dopants and an organic solvent unless the effect of the present invention is impaired.

[0041]

Examples of such other dopants include inorganic acids (e.g., sulfuric acid and nitric acid), halogen ions (e.g., iodine, bromine, and chlorine), halide ions (e.g., tetrafluoroboron and perchloric acid), quinone compounds [e.g., chloranilic acid, p-chloranil, p-benzoquinone, p-quinonedioxime, dichlorodicyanoquinone (DDQ), p-naphthoquinone, anthraquinone, chloroanthraquinone, and p-toluquinone), alkyl-substituted organic sulfonic acid ions (e.g., methanesulfonic acid and dodecylsulfonic acid), cyclic sulfonic acid ions (e.g., camphorsulfonic acid ion), alkyl-substituted or unsubstituted benzenemono- or

benzenedi-sulfonic acid ions (e.g., benzenesulfonic acid, paratoluene sulfonic acid, dodecylbenzenesulfonic acid, and benzenedisulfonic acid), alkyl-substituted or unsubstituted ions of naphthalenesulfonic acids having 1 to 4 sulfonic acid groups (e.g., 2-naphthalenesulfonic acid and 1,7-naphthalenedisulfonic acid), an anthracenesulfonic acid ion, an anthraquinonesulfonic acid ion, alkyl-substituted or unsubstituted biphenylsulfonic acid ions (e.g., alkylbiphenylsulfonic acid and biphenyldisulfonic acid), and substituted or unsubstituted aromatic polymeric sulfonic acid ions (e.g., polystyrenesulfonic acid and naphthalenesulfonic acid-formalin condensates).

[0042]

The use amount of such other dopants is preferably 0 to 1100% by weight, and more preferably 10 to 600% by weight relative to the substituted polythiophene (P).

[0043]

The conductive composition (A) of the present invention may further comprise an organic solvent as stated above. A conductive coating film can be produced by applying the conductive composition (A) to a substrate, and then removing the organic solvent by heating as necessary. In order to obtain a homogenous solution containing no precipitate, it is preferred to use as the organic solvent a good solvent of the substituted polythiophene (P) and a good solvent of the dopant

in admixture.

[0044]

Examples of the good solvent of the substituted polythiophene (P) include chlorine-containing, amide-based, ether-based, aromatic hydrocarbon-based, alcohol-based, ketone-based, and sulfur-containing solvents having 1 to 10 carbon atoms, and preferred are chloroform, methylene chloride, dimethylformamide, N-methylpyrrolidone, tetrahydrofuran (hereinafter abbreviated as THF), 1,3-dioxolane, toluene, methanol, acetone, methyl ethyl ketone, γ -butyrolactone, cyclopentanone, cyclohexanone, dimethyl sulfoxide, and mixtures thereof.

[0045]

The content of the good solvent of the substituted polythiophene (P) in the solution prepared by mixing the good solvent and the substituted thiophene (P) is preferably 0 to 99% by weight, and more preferably 50 to 98% by weight in the solution.

[0046]

Examples of the good solvent of the dopant include methanol, ethanol, 2-propanol, ethylene glycol, N-methylpyrrolidone, THF, γ -butyrolactone, and cyclopentanone. Of these, preferred from the viewpoint of dissolution stability are methanol, ethanol, 2-propanol, and γ -butyrolactone.

[0047]

The content of the good solvent of the dopant in the solution prepared by mixing the good solvent and the dopant is preferably 0 to 99% by weight, and more preferably 50 to 98% by weight in the solution.

[0048]

In order to obtain a homogeneous solution in mixing the substituted polythiophene (P) and the dopant, it is preferable to prepare a solution of the substituted polythiophene (P) in a solvent and a solution of the dopant in a solvent, respectively, and then mix the solutions.

[0049]

When producing a conductive coating film by using the conductive composition (A) of the present invention, it is necessary to remove the solvent. In the case of a low-boiling point solvent, the solvent is removed by air drying at normal temperature or heat drying by air circulation, whereas in the case of a high-boiling point solvent, heat drying using a vacuum dryer is preferred.

[0050]

The conductive composition (A) of the present invention is suitable especially for an electrode for solid electrolyte capacitors. A capacitor having an electrode (cathode) produced by forming a porous film by etching an oxidized film of aluminum or the like and then forming a conductive polymer layer on a surface thereof has been used as a solid electrolyte

capacitor. However, conventional methods, such as a method of applying a dispersion liquid containing a precursor monomer of a conductive polymer and a method of applying a solution prepared by dissolving a polypyrrole as a conductive polymer in a solvent while using dodecylbenzenesulfonic acid as a dopant, are problematic in that capacitor production efficiency is very low, that the capacitance cannot be increased efficiently, and that withstand voltage drops or leak current increases due to the corrosion of an electrode because the dopant is an acid.

[0051]

In contrast to this, since the conductive composition (A) of the present invention has been fully dissolved in an organic solvent and is high in electroconductivity, it is possible to impregnate a porous film with a conductive polymer by a simple process, thereby efficiently increasing the capacitance, and there is no fear of corrosion because the dopant is not an acid.

[0052]

An electrode for a solid electrolyte capacitor that is high in withstand voltage and little in leak current can be obtained by applying the conductive composition (A) of the present invention to a substrate and then performing heat treatment.

[0053]

Examples of the method for applying the conductive composition (A) to the substrate include a spin coating method,

a drop casting method, a dip coating method, and a method of immersing the substrate in the conductive composition (A). Examples of the substrate include plastics, glass, metal, rubber, ceramics, paper and the like.

[0054]

From the viewpoint of electroconductivity, the thickness of the film that is to be formed and dried on a substrate surface using the conductive composition (A) is preferably 0.05 to 100 μm , and more preferably 0.1 to 50 μm . If the coating film is thinner than 0.05 μm , sufficient electroconductivity may not be obtained. A thickness exceeding 100 μm may cause a problem, for example, that cracking or peeling occurs easily in film forming.

[0055]

In order to obtain a conductive coating film with high electroconductivity using the conductive composition (A) of the present invention, the heat treating temperature is preferably 100 to 190°C, and more preferably 110 to 170°C. In the case of a temperature lower than 100°C, sufficient strength and electroconductivity may not be obtained. In the case of a temperature higher than 190°C, electroconductivity may deteriorate.

[0056]

The heating time, which may be selected appropriately according to the heating temperature and the concentration of

the substituted polythiophene (P) in the conductive composition (A), is usually 0.5 to 8 hours, and preferably 1 to 4 hours. If the heating time becomes shorter, the electroconductivity of the conductive coating film to be obtained from the conductive composition (A) may be insufficient.

[0057]

The conductive composition (A) of the present invention is useful because it is lowly corrosive since the dopant contained therein is not an acid and is superior in electroconductivity, it can produce a conductive coating film by only simple application thereof. In particular, it is useful because it allows the capacitance of a capacitor to be increased efficiently through the impregnation of a porous film with a conductive polymer by a simple process and it can produce a solid electrolyte capacitor with high withstand voltage and little leak current.

EXAMPLES

[0058]

The present invention is further described by means of the following examples and comparative examples, but the invention is not limited thereto. In the following, "part(s)" means "part(s) by weight".

[0059]

<Production	Example	1>:	Synthesis	of
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poly[3-(1,4,7,10-tetraoxaundecyl)thiophene] (P-1)

(1) Synthesis of 3-(1,4,7,10-tetraoxaundecyl)thiophene:

In 50 parts of N,N-dimethylformamide was dispersed 6.0 parts of sodium hydride (dispersed in paraffin in a concentration of 60% by weight), and then 36.9 parts of triethylene glycol monomethyl ether was dropped thereto. Bubbles were generated in the reaction solution and the solution became cloudy. When the generation of bubbles was settled, 24.5 parts of 3-bromothiophene and 2.0 parts of copper(I) bromide were added in this order to the reaction solution. The reaction solution was heated to 110°C and a reaction was carried out for 2 hours. After the completion of the reaction, the reaction solution was allowed to cool down to room temperature. Following addition of 50 parts of a 1 mol/L aqueous ammonium chloride solution, the mixture was moved to a separatory funnel using 50 parts of ethyl acetate and then the aqueous layer was separated. Further, the organic layer was washed twice with 30 parts of distilled water and then ethyl acetate was distilled off, so that 34.0 parts of 3-(1,4,7,10-tetraoxaundecyl)thiophene was obtained.

[0060]

(2) Synthesis of 2,5-dibromo-3-(1,4,7,10-tetraoxaundecyl)thiophene:

In 40 parts of THF were dissolved 7.4 parts of the

aforementioned 3-(1,4,7,10-tetraoxaundecyl)thiophene and 10.7 parts of N-bromosuccinimide, which were then allowed to react at room temperature for 2 hours. A precipitate was removed with a glass filter using 50 parts of ethyl acetate, and THF and ethyl acetate were then distilled off. By purifying the resulting mixture with a silica gel column, 10.5 parts of 2,5-dibromo-3-(1,4,7,10-tetraoxaundecyl)thiophene was obtained.

[0061]

(3) Synthesis of poly[3-(1,4,7,10-tetraoxaundecyl)thiophene]:

After dissolving 8.1 parts of the aforementioned 2,5-dibromo-3-(1,4,7,10-tetraoxaundecyl)thiophene in 150 parts of THF, 21 parts of 1 mol/L methylmagnesium bromide solution in THF was added thereto and then a reaction was performed at 75°C for 30 minutes. To the reaction solution was added 0.1 parts of [1,3-bis(diphenylphosphino)propane]-dichloronickel (II), and then a reaction was performed for additional 5 hours still at 75°C. After allowing the reaction solution to cool down to room temperature, 20 parts of methanol was added thereto. After distilling off a solvent, the reaction mixture was moved to a Soxhlet extractor and was washed with 150 parts of methanol and 150 parts of hexane in this order. Finally, the residue was subjected to extraction using 150 parts of chloroform and then

the solvent was distilled off, so that 3.1 parts of poly[3-(1,4,7,10-tetraoxaundecyl)thiophene] (P-1) was obtained. The regioregularity calculated by the above-described method using $^1\text{H-NMR}$ was 96.3%.

[0062]

<Production Example 2>: Synthesis of poly[3-(1,4,7,10,13,16,19-heptaoxaeicosyl)thiophene] (P-2)

Experimental operations were carried out which were the same as those of Production Example 1 except for exchanging triethylene glycol monomethyl ether in (1) of Production Example 1 for hexaethylene glycol monomethyl ether (produced by Tokyo Chemical Industry Co., Ltd.), so that 2.9 parts of poly[3-(1,4,7,10,13,16,19-heptaoxaeicosyl)thiophene] (P-2) having a regioregularity of 95.1% was obtained.

In exchanging triethylene glycol monomethyl ether for hexaethylene glycol monomethyl ether, the experimental operations were carried out with the amounts of the raw materials were adjusted so that the molar ratio of the reaction components and the weight ratio of the non-reaction components (solvent, etc.) might become equal to those in Production Example 1.

[0063]

<Production Example 3>: Synthesis of poly(3-heptyloxythiophene) (P-3)

Experimental operations were carried out which were the

same as those of Production Example 1 except for exchanging triethylene glycol monomethyl ether in (1) of Production Example 1 for 1-heptanol, so that 2.7 parts of poly(3-heptyloxythiophene) (P-3) having a regioregularity of 95.4% was obtained.

[0064]

<Production Example 4>: Synthesis of poly{3-(2,5-dioxaheptyl)thiophene} (P-4)

(1) Synthesis of 3-bromomethylthiophene:

After dissolving 5 parts (50.9 mmol) of 3-methylthiophene [produced by Tokyo Chemical Industry Co., Ltd.], 9.97 parts (56.0 mmol) of N-bromosuccinimide, and 0.12 parts (0.50 mmol) dibenzoyl peroxide [produced by Tokyo Chemical Industry Co., Ltd.] in 30 parts of benzene, the temperature was raised to 100°C and then a reaction was carried out for 4 hours. After the completion of the reaction, the resultant was allowed to cool down to room temperature. Following addition of 30 parts of a 1M aqueous sodium thiosulfate solution, the mixture was moved to a separatory funnel and then the aqueous layer was separated. Further, the organic layer was washed twice with 30 parts of distilled water and then benzene was distilled off, so that 6.32 parts (35.7 mmol) of 3-bromomethylthiophene was obtained.

[0065]

(2) Synthesis of 3-(2,5-dioxaheptyl)thiophene:

In 15 parts of THF was dissolved 3.54 parts (39.3 mmol)

[0066]

In THF were dissolved 5.68 parts (30.5 mmol) of the aforementioned 3-(2,5-dioxaheptyl)thiophene and 11.9 parts (67.1 mmol) of N-bromosuccinimide, which were then allowed to react at room temperature for 2 hours. A precipitate was removed with a glass filter using 50 parts of ethyl acetate, and THF and ethyl acetate were then distilled off. By purifying the resulting mixture with a silica gel column, 8.11 parts (23.6 mmol) of 2,5-dibromo-3-(2,5-dioxaheptyl)thiophene was

obtained.

[0067]

(4) Synthesis of poly{3-(2,5-dioxaheptyl)thiophene}:

After dissolving 8.11 parts (23.6 mmol) of the aforementioned 2,5-dibromo-3-(2,5-dioxaheptyl)thiophene in 30 parts of THF, 25 parts of methylmagnesium bromide solution in THF was added thereto and then a reaction was performed at 75°C for 30 minutes. To the reaction solution was added 0.127 parts of [1,3-bis(diphenylphosphino)propane]-dichloronickel (II), and then a reaction was performed for additional 2 hours still at 75°C. After allowing the reaction solution to cool down to room temperature, 5 parts of methanol was added. The reaction mixture was moved to a Soxhlet extractor and was washed with 150 parts of methanol and 150 parts of hexane in this order. Finally, the residue was subjected to extraction using 150 parts of chloroform and then the solvent was distilled off, so that 2.85 parts of poly{3-(2,5-dioxaheptyl)thiophene} (P-4) having a regioregularity of 94.6% was obtained.

[0068]

<Production Example 5>: Synthesis of poly(3-dodecylthiophene) (P-5)

Experimental operations were carried out which were the same as those of Production Example 1 except for exchanging 2,5-dibromo-3-(1,4,7,10-tetraoxaundecyl)thiophene in (3) of Production Example 1 for 2,5-dibromo-3-dodecylthiophene

(produced by Aldrich), so that 3.5 parts of poly(3-dodecylthiophene) (P-5) having a regioregularity of 96.4% was obtained.

[0069]

<Examples 1 to 16>

Conductive compositions (A-1) to (A-16) of the present invention were obtained by mixing the compounded parts given in Table 1 of the substituted polythiophenes (P-1) to (P-5) obtained in Production Examples 1 to 5, the sulfur trioxide complexes and the organic solvents given in Table 1.

[0070]

[Table 1]

Conductive composition		Examp le 1	Examp le 2	Examp le 3	Examp le 4	Examp le 5	Examp le 6	Examp le 7	Examp le 8	Examp le 9	Examp le 10	Examp le 11	Examp le 12	Examp le 13	Examp le 14	Examp le 15	Examp le 16	Comparative Example 1	Comparative Example 2	Comparative Example 3	
		(A-1)	(A-2)	(A-3)	(A-4)	(A-5)	(A-6)	(A-7)	(A-8)	(A-9)	(A-10)	(A-11)	(A-12)	(A-13)	(A-14)	(A-15)	(A-16)	(A'-1)	(A'-2)	(A'-3)	
Compounded parts (part (s) by mass)	(P-1)	1.0	1.0	1.0	1.0	1.0	1.0	1.0	-	-	-	1.0	1.0	1.0	-	-	-	1.0	-	1.0	
	Substituted polythiophene (P)	-	-	-	-	-	-	-	-	-	-	-	-	-	1.0	1.0	1.0	-	-	-	
	(P-2)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	
	(P-3)	-	-	-	-	-	-	-	1.0	-	-	-	-	-	-	-	-	-	-	-	
	(P-4)	-	-	-	-	-	-	-	-	1.0	-	-	-	-	-	-	-	-	-	-	
	(P-5)	-	-	-	-	-	-	-	-	-	1.0	-	-	-	-	-	-	-	-	-	
	PEDOT/PSS aqueous dispersion	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	2.4	-	
	Sulfur trioxide-N,N-dimethylformamide complex	2.7	1.3	2.7	-	-	2.7	0.7	1.3	2.7	0.7	1.3	2.7	0.7	1.3	2.7	0.7	0.7	-	-	-
	Sulfur trioxide-pyridine complex	-	-	-	2.7	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	Sulfur trioxide-triethylamine complex	-	-	-	-	2.7	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Organic solvent	Iron p-toluenesulfonate	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	2.7	
	Chloroacetic acid	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.3	-	-	
	1,3-Dioxolane	49.0	32.3	32.3	32.3	32.3	32.3	32.3	-	-	-	99.0	99.0	99.0	-	-	-	30	-	32.3	
	γ-Butyrolactone	-	-	-	-	-	-	-	131.7	131.0	129.7	32.7	32.0	30.7	1.4	1.4	1.4	-	-	-	
	Methanol	14.0	9.8	8.4	8.4	8.4	-	-	-	-	-	-	-	-	5.3	-	-	-	-	8.4	
	Dimethylformamide	-	-	-	-	-	8.4	-	-	-	-	-	-	-	-	-	-	-	-	-	
	N-methylpyrrolidone	-	-	-	-	-	-	8.4	-	-	-	-	-	-	-	5.3	-	-	-	-	
	Cyclopentanone	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	5.3	-	-	-	
	Water	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	97.6	-	
	Result of electroconductivity evaluation	Thickness (μm)	0.43	0.79	1.81	0.95	1.34	1.33	1.9	0.31	0.14	0.14	0.17	0.19	0.21	2.25	6.17	8.81	1.12	1.32	1.08
Capacitor evaluation	Electroconductivity evaluation	Electroconductivity S/cm)	724.4	902.2	403.1	86.6	19.3	371.8	337	157.2	214.6	250.8	239.1	311.6	385.5	192.4	35.5	68.6	0.1	86.5	0.8
	Result of corrosivity evaluation	Leakage	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	X	X	X
	Electrostatic capacitance (μF/120 Hz)	4.1	4.1	4.1	4.1	4.1	4.1	4.0	3.9	3.8	3.9	4.0	4.1	4.1	4.0	4.1	4.0	-	0.44	0.61	
	Internal resistance (mΩ/100 kHz)	15	12	14	22	28	11	17	18	20	12	12	14	15	19	20	19	-	88000	75000	
Withstand voltage (V)		30	28	32	25	27	31	30	25	24	26	30	32	31	28	27	29	-	17	18	

[0071]

<Comparative Example 1>

A conductive composition (A'-1) for comparison was obtained by mixing 1.0 part of substituted polythiophene (P-1), 0.3 parts of chloranilic acid, and 30.0 parts of 1,3-dioxolane as an organic solvent.

[0072]

<Comparative Example 2>

"PEDOT/PSS" (a conductive polymer prepared by polymerizing Baytron-P (3,4 -ethylenedioxythiophene produced by H.C. Starck) in an aqueous high molecular weight polystyrene sulfonic acid solution), which was known as an aqueous dispersion of a polythiophene, was used as it was as a conductive composition (A'-2) for comparison.

[0073]

<Comparative Example 3>

A conductive composition (A'-3) for comparison was obtained by mixing 1.0 part of substituted polythiophene (P-1), 2.7 parts of iron p-toluenesulfonate as well as 32.3 parts of 1,3-dioxolane and 8.4 parts of methanol as an organic solvent.

[0074]

Conductive coating films were prepared and evaluation of the electroconductivity thereof was carried out by the following methods using the conductive compositions (A-1) to (A-16) of Examples 1 to 16 and the conductive compositions

(A'-1) to (A'-3) for comparison. Results are shown in Table 1.

[0075]

[Method for preparing conductive coating film]

Each of the conductive compositions (A-1) to (A-16) of Examples 1 to 16 and the conductive compositions (A'-1) to (A'-3) for comparison was applied to a glass substrate in a 3 cm × 7 cm rectangular pattern with a doctor blade, followed by drying under reduced pressure at room temperature for 30 minutes and subsequently heating on a hot plate at 170°C for 60 minutes, so that a conductive coating film was obtained.

[0076]

[Method for electroconductivity evaluation]

The surface resistance of a resulting conductive coating film was measured in accordance with "Testing method for resistivity of conductive plastics with a four-point probe array" of JIS K7194.

Then, the thickness of the conductive coating film was measured by using a laser microscope (VK-8700 manufactured by KEYENCE CORP.), and the electroconductivity of the conductive coating film was calculated from the surface resistance and the thickness.

[0077]

Each of the conductive compositions (A-1) to (A-16) of Examples 1 to 16 and the conductive compositions (A'-1) to

(A'-3) for comparison in an amount of 10 mL was put into a glass container and then a glass substrate with ITO (1 cm × 1 cm × 0.1 mm) was immersed into the solution, followed by sealing the glass container. After storage under conditions of a storage temperature of 25°C and a storage time of 150 hours, the glass substrate with ITO was taken out and then washed with THF. The corrosion state of the surface of ITO of the glass substrate with ITO after washing was observed by a microscope (digital microscope VHX manufactured by KEYENCE CORP.) and was evaluated on the basis of the following criteria. The results are shown in Table 1.

<Corrosivity evaluation criteria>

○ (No corrosion is observed.)

× (Corrosion is observed.)

It was shown that the conductive composition of the present invention fails to have corrosivity as shown in Table 1.

[0078]

[Method of capacitor characteristic evaluation]

(1) Preparation of dielectric film on anode

An aluminum etched foil (size: 4 × 3.3 mm) as an anode metal was immersed in a 3% by weight aqueous ammonium adipate solution, voltage was increased from 0 V to 40 V under a condition of 0.53 mA/sec by using a constant-current constant-voltage power supply, and then chemical conversion treatment was

performed by applying a constant voltage of 40 V for 40 minutes, so that a dielectric film made of an oxidized coating film was formed on a surface of the aluminum etched foil. This was washed in running deionized water for 10 minutes and then was dried at 105°C for 5 minutes, so that an anode composed of an anode metal and a dielectric film was prepared. The resulting anode was immersed in the aforementioned aqueous ammonium adipate solution and an electrostatic capacitance was measured at 120 Hz. The measurement 4.2 μ F was determined as a theoretical electrostatic capacitance.

[0079]

(2) Preparation of electrode for solid electrolyte capacitor

Anodes were immersed in the conductive compositions (A-1) to (A-16) and (A'-1) to (A'-3) and then were pulled up, followed by drying under reduced pressure at room temperature for 30 minutes, so that electrolyte layers were formed and thereby electrodes for solid electrolyte capacitors were prepared.

(3) Preparation of an electrolyte capacitor

On each of the electrolyte layers obtained above, a carbon paste ["Varniphite FU" produced by Nippon Graphite Industries, Ltd.] was applied and then dried, and thereafter a silver paste ["Everyohm ME" produced by Nippon Graphite Industries, Ltd.] was further applied, so that a cathode was formed. A lead was pulled out from the silver paste and a terminal was connected

thereto.

[0080]

(4) Measurement and evaluation

The electrostatic capacitance at 120 Hz and the internal resistance at 100 kHz of the resulting electrolyte capacitor were measured using an LCR meter, and then the occurrence of leakage and withstand voltage were evaluated on the following criteria.

<Criteria of leakage evaluation>

A case where a leak current did not decrease and neither an electrostatic capacitance nor an internal resistance was measured successfully in the measurement with the LCR meter was evaluated as "×" and a case where a leak current decreased and both an electrostatic capacitance and an internal resistance were measured successfully was evaluated as "○".

<Criteria of withstand voltage evaluation>

Voltage was applied in a low current mode of 0.2 mA by using a DC power unit [GP0650-05R manufactured by Takasago Ltd.] and was elevated automatically, and the voltage detected just before voltage dropped suddenly due to discharge was defined as a withstand voltage.

[0081]

The solid electrolyte capacitors using the conductive compositions of the present invention each afforded an electrostatic capacitance close to the theoretical value (4.2

μF) while maintaining a low internal resistance necessary as a capacitor. Conversely, in the capacitor using the conductive composition of Comparative Example 1, corrosion was generated inside the electrode because the dopant was an acid, and there was so great leakage that it could not be measured. In the capacitor using the conductive composition of Comparative Example 2 for solid electrolyte capacitors, since the conductive polymer existed as a dispersion in a solution, clogging occurred inside pores, so that the conductive polymer has not penetrated well. Therefore, internal resistance was high and a capacitance as large as only about 1/10 the theoretical electrostatic capacitance was obtained. In Comparative Example 3, capacitance was insufficient and internal resistance was high. Moreover, the withstand voltage was also lower in comparison to Example 1 to 16.

As shown in Table 1, it was indicated that the conductive composition of the present invention was high in electroconductivity.

INDUSTRIAL APPLICABILITY

[0082]

The conductive composition (A) of the present invention are so lowly corrosive that it can be applied to metal or the like which are prone to be corroded and the conductive coating film has high electroconductivity, it can be expected to be

applied to various conductive functional materials. Especially, it is useful as an electrode for a solid electrolyte capacitor.

CLAIMS

1. A conductive composition(A) comprising a sulfur trioxide complex and a substituted polythiophene (P) having thiophene repeating units at least some of which are each a thiophene repeating unit (α) substituted at the 3-position and/or the 4-position of its thiophene ring with at least one group selected from the group consisting of

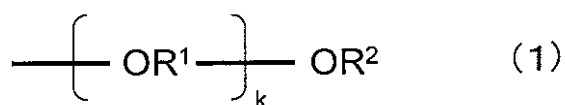
(a) a polyether group represented by formula (1) given below,

(b) an alkoxy group having 1 to 15 carbon atoms,

(c) an alkoxyalkyl group having 2 to 19 carbon atoms, and

(d) an alkyl group having 1 to 15 carbon atoms or an alkyl group of which a hydrogen atom has been substituted with the polyether group (a);

[Chem. 1]

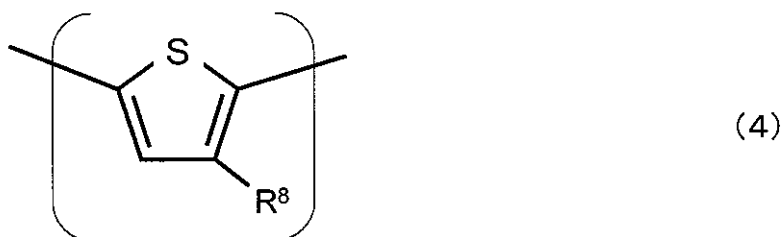
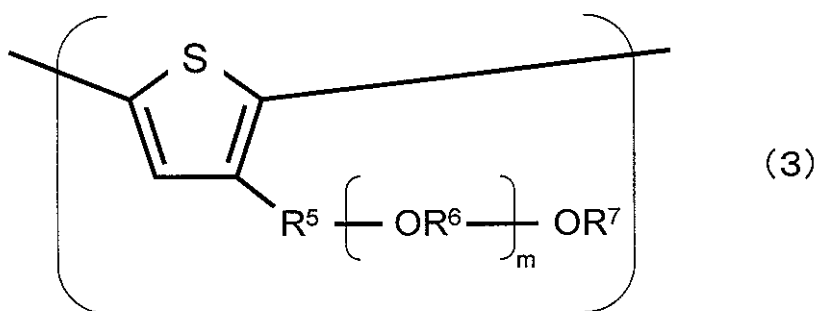
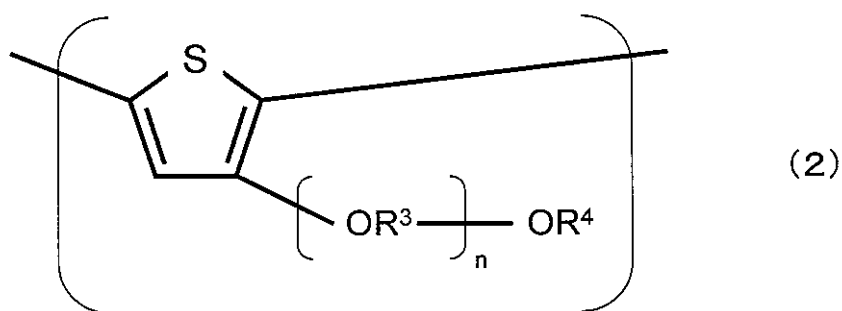


wherein OR^1 represents an oxyalkylene group having 2 to 4 carbon atoms, R^2 represents an alkyl group having 1 to 15 carbon atoms, and k is an integer of 1 to 9.

2. The conductive composition according to claim 1, wherein the thiophene repeating unit (α) is a repeating unit ($\alpha 1$) represented by formula (2), a repeating unit ($\alpha 2$)

represented by formula (3), or a repeating unit ($\alpha 3$) represented by formula (4);

[Chem. 2]



wherein OR^3 and OR^6 each independently represent an oxyethylene group or an oxypropylene group, R^4 , R^7 , and R^8 each independently represent a linear or branched alkyl group having 1 to 12 carbon atoms, R^5 represents a linear or branched alkylene group having 1 to 4 carbon atoms, and n and m are each independently an integer of 0 to 5.

3. The conductive composition according to claim 2, wherein the repeating unit ($\alpha 1$) is one in which OR^3 in formula (2) is an oxyethylene group, and R^4 is a linear or branched alkyl group having 3 to 12 carbon atoms when n is 0, and R^4 is a linear or branched alkyl group having 1 to 6 carbon atoms when n is 1 or more; the repeating unit ($\alpha 2$) is one in which R^5 in formula (3) is a linear or branched alkylene group having 1 to 3 carbon atoms, OR^6 is an oxyethylene group and R^7 is a linear or branched alkyl group having 3 to 12 carbon atoms when m is 0, and R^7 is a linear or branched alkyl group having 1 to 6 carbon atoms when m is 1 or more; and the repeating unit ($\alpha 3$) is one in which R^8 in formula (4) is a linear or branched alkyl group having 3 to 12 carbon atom.

4. The conductive composition according to any one of claims 1 to 3, wherein the content of the thiophene repeating unit (α) in the substituted polythiophene (P) is 50 to 100% by weight of the substituted polythiophene (P).

5. The conductive composition according to any one of claims 1 to 4, wherein the regioregularity defined by the percentage of Head-to-Tail-Head-to-Tail linkages in the substituted polythiophene (P) is 90% or more.

6. The conductive composition according to any one of claims 1 to 5, wherein the sulfur trioxide complex is at least one sulfur trioxide complex selected from the group consisting of a sulfur trioxide-N,N-dimethylformamide complex, a sulfur trioxide-pyridine complex, and a sulfur trioxide-triethylamine complex.

7. The conductive composition according to any one of claims 1 to 6, wherein the content of the sulfur trioxide complex based on the weight of the substituted polythiophene (P) is 5 to 300% by weight.

8. An electrode for a solid electrolyte capacitor produced by using the conductive composition according to any one of claims 1 to 7.

9. A solid electrolyte capacitor produced by using the conductive composition according to any one of claims 1 to 7.

10. A process for producing a conductive coating film comprising applying the conductive composition according to any one of claims 1 to 7 to a substrate and then heat-treating it.