

DESCRIPTION

Title of Invention: SOLID ELECTROLYTIC CAPACITOR AND METHOD FOR PRODUCING SAME

Technical Field

[0001]

The present invention relates to a solid electrolytic capacitor having a solid electrolyte layer, and more particularly to a solid electrolytic capacitor and a method for producing the same, the solid electrolytic capacitor containing as the solid electrolyte layer a conductive polymer layer that exhibits high conductivity and having excellent electric properties.

Background Art

[0002]

Known as a material for forming a solid electrolyte used in a solid electrolytic capacitor are an inorganic conductive material as typified by manganese dioxide and an organic conductive material such as 7,7,8,8-tetracyanoquinodimethane (TCNQ) complex.

Besides, widely commercialized is a solid electrolytic capacitor having as the solid electrolyte a conductive polymer material that is more excellent in electric properties than these solid electrolyte-forming materials.

[0003]

As such a conductive polymer material, conductive polymer made by polymerization of 3,4-ethylenedioxythiophene (hereinafter abbreviated to "EDOT") monomers is known broadly.

As this EDOT has a slow polymerization rate and allows to form

a conductive polymer layer that has good adhesion to the anode dielectric oxide film, it is useful as a material for forming a solid electrolyte layer of the solid electrolytic capacitor.

[0004]

However, electronic devices in these days are required to save more power and support higher frequencies, and solid electrolytic capacitors used in these electronic devices are also required to further improve electric properties, for example, to reduce the size, increase the capacity and reduce the Equivalent Series Resistance (hereinafter abbreviated as "ESR").

The electric properties of the solid electrolytic capacitor largely depend on a material used for forming the solid electrolyte and its forming method. There are hopes for development of conductive monomers that are more excellent than the conventional EDOT and a new method for forming a solid electrolyte layer.

[0005]

Against this backdrop, a solid electrolytic capacitor is known as related art which has 3-alkyl-4-alkoxythiophene polymer as solid electrolyte. As this polymer is used, the obtained solid electrolytic capacitor is allowed to have excellent electric properties even in high-frequency range (PL1).

[0006]

Further proposed is a solid electrolytic capacitor that uses as a solid electrolyte molecules obtained by polymerizing alkylenedioxythiophene derivative of which a part substitutes for an alkoxy group.

With use of this polymer, it is possible to suppress crystallization of polymerization oxidant remaining in the polymer and to reduce leakage current of the solid electrolytic capacitor

(see PL2 below).

Citation List

Patent Literature

[0007]

PL1: Japanese Patent Application Laid-Open No. 2001-332453

PL2: Japanese Patent Application Laid-Open No. 2004-096098

Summary of Invention

Technical Problem

[0008]

However, even for the polymers disclosed in the above-mentioned publications, it is difficult to have sufficient electric properties or heat resistance. There are demands for improvement in electric properties and heat resistance of the solid electrolytic capacitor.

Meanwhile, in order to increase the capacitance of the solid electrolytic capacitor, there are proposed a foil type of using a wound or laminated aluminum foil as an anode element, the surface of the aluminum foil being roughened by etching and a sintered element type of sintering and molding metal fine particles into a porous body thereby to achieve larger capacitance. In the sintered element type, the particle diameter of the metal fine particles becomes smaller for the purpose of increasing the capacitance and its CV product (product of voltage and capacitance per sintered element 1g) is 100,000 $\mu\text{FV/g}$ or more.

Further, in these days, in order to enhance the performance, polypyrrole and PEDOT (polyethylenedioxythiophene) are used in the solid electrolyte. These are polymerized by chemical oxidative polymerization or electropolymerization. However, pores of the

porous sintered element tend to finer and it is difficult to fill these pores with polymerized polypyrrole or PEDOT.

[0009]

The present invention aims to provide a solid electrolytic capacitor and a method for producing the same, the solid electrolytic capacitor that has excellent heat-resistance and electric properties, showing a high capacitance and a low ESR.

Solution to Problem

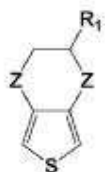
[0010]

The inventors of the present invention studied dedicatedly, and finally have found that the objective of the present invention can be achieved by a solid electrolytic capacitor containing, as a solid electrolyte, molecules obtained by polymerizing a compound expressed by the following formula [1] and completed the present invention. The present invention is described specifically below.

[0011]

The first aspect of the present invention is a solid electrolytic capacitor comprising, as solid electrolyte, molecules obtained by polymerizing a compound expressed by a formula [1] (in the formula, R₁ represents a straight-chain or branched-chain alkyl group with from 1 to 6 carbon atoms and Z represents oxygen atom or sulfur atom, independently).

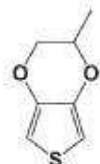
[1]



[0012]

The second aspect of the present invention is a solid electrolytic capacitor comprising, as solid electrolyte, molecules obtained by polymerizing at least one of compounds expressed by formulas [2] and [3].

[2]



[3]



[0013]

The third aspect of the present invention is the solid electrolytic capacitor of the second aspect of the present invention, wherein the molecules are obtained by polymerizing the compound expressed by the formula [2].

[0014]

The fourth aspect of the present invention is the solid electrolytic capacitor of the second aspect of the present invention, further comprising:

a porous body, as an anode, obtained by sintering valve-action metal particles;

a dielectric oxide film formed on a surface of the anode;

solid electrolyte containing molecules obtained by polymerizing the compound expressed by at least one of the formulas [2] and [3] on a surface of the dielectric oxide film; and

a cathode having a carbon layer and a silver layer formed on the molecules.

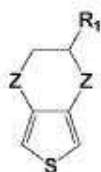
[0015]

The fifth aspect of the present invention is the solid electrolytic capacitor of the fourth aspect of the present invention, wherein the valve-action metal particles used in the porous body obtained by sintering of the valve-action metal particles contain at least one of tantalum metal particles and niobium metal particles, and a CV product per unit mass is 20000 $\mu\text{FV/g}$ or more.

[0016]

The sixth aspect of the present invention is a method for producing a solid electrolytic capacitor comprising a step of obtaining molecules by polymerizing a compound expressed by a formula [1] and forming the molecules on valve-action metal where a dielectric oxide film is formed (in the formula, R₁ represents a straight-chain or branched-chain alkyl group with from 1 to 6 carbon atoms and Z represents oxygen atom or sulfur atom, independently).

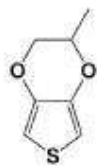
[1]



[0017]

The seventh aspect of the present invention is a method for producing a solid electrolytic capacitor comprising a step of obtaining molecules by polymerizing at least one of compounds expressed by formulas [2] and [3] and forming the molecules on valve-action metal where a dielectric oxide film is formed.

[2]



[3]



[0018]

The eighth aspect of the present invention is the method of the sixth or seventh aspect of the present invention, wherein the step of forming the molecules on the valve-action metal where the dielectric oxide film is formed comprises performing polymerization by bringing (A) at least one selected from a group consisting of compounds expressed by formulas [1] to [3], (B) a dopant, and (C) an oxidant into contact with each other in a liquid phase.

[0019]

The ninth aspect of the present invention is the method of the eighth aspect of the present invention, wherein (B) the dopant and (C) the oxidant are replaced with a compound having properties of both (B) the dopant and (C) the oxidant.

[0020]

The tenth aspect of the present invention is the method of the ninth aspect of the present invention, wherein the compound having properties of both (B) the dopant and (C) the oxidant is organic sulfonic acid iron(III) salt and the liquid phase contains 40 to 70 wt% of the organic sulfonic acid iron(III) salt.

[0021]

The eleventh aspect of the present invention is the method of the seventh aspect of the present invention, wherein a porous body obtained by sintering valve-action metal particles is used as an anode and the method further comprises:

forming the dielectric oxide film on a surface of the anode;

forming the molecules obtained by polymerization of at least one of the compounds expressed by the formulas [2] and [3], on the anode where the dielectric oxide film is formed; and

forming a cathode containing a carbon layer and a silver layer on the molecules.

[0022]

The twelfth aspect of the present invention is the method of the eleventh aspect of the present invention, wherein the step of forming the molecules on the anode where the dielectric oxide film is formed comprises: bringing (A) the at least one selected from the group consisting of the compounds expressed by the formulas [1] to [3] and (C) the oxidant into contact with each other in the liquid phase to conduct chemical oxidative polymerization.

Advantageous Effects of Invention

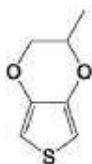
[0023]

According to the present invention, it is possible to provide a solid electrolytic capacitor that has excellent heat-resistance, a high capacitance and a low ESR.

Besides, when the molecules used as the solid electrolyte are obtained by polymerizing a compound expressed by at least one of the following formulas [2] and [3], the polymerization rate of these monomers is relatively slow and therefore, it is possible to fill

in pores of a porous body obtained by sintering valve-action metal particles that are finely porous.

{ 2 }



{ 3 }



With this structure, it is possible to provide a solid electrolytic capacitor that has excellent heat-resistance, a high capacitance and a low ESR.

Brief Description of Drawings

[0024]

Fig. 1 is a graph of the carbon number of the horizontal axis of a substituent of EDOT indicated by the horizontal axis and the polymerization rate (seconds) indicated by the vertical axis (Examples 4 to 6 and Comparative Example 1 and 2);

Fig. 2 is a graph of the carbon number of the horizontal axis of a substituent of EDOT indicated by the horizontal axis and the ESR ($m\Omega$) indicated by the vertical axis (Examples 7 to 9 and Comparative Example 4 and 7); and

Fig. 3 is a schematic cross sectional view for explaining the structure of a solid electrolytic capacitor according to Example 10 of the present invention.

Description of Embodiments

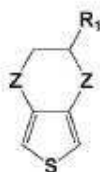
[0025]

The present invention will be described in detail below.

The present invention provides a solid electrolytic capacitor containing, as a solid electrolyte, molecules obtained by polymerizing a compound expressed by the following formula [1].

[0026]

(1)



[0027]

In the above-mentioned formula [1], R1 represents a straight-chain or branched-chain alkyl group with from 1 to 6 carbon atoms. Z represents oxygen atom or sulfur atom, independently.

[0028]

The straight-chain or branched-chain alkyl group with from 1 to 6 carbon atoms includes, for example, methyl group, ethyl group, n-propyl group, iso-propyl group, n-butyl group, iso-butyl group, sec-butyl group, t-butyl group, n-pentyl group, iso-pentyl group, 1-methylbutyl, 1-ethylpropyl group, 1, 2-dimethylpropyl group, 1, 1-dimethylpropyl group, neopentyl group, n-hexyl group and so on.

Among those groups, a straight-chain or branched-chain alkyl group with from 1 to 3 carbon atoms is preferably used, which is specifically, methyl group, ethyl group, n-propyl group, iso-propyl group, or more preferably, methyl group, ethyl group, or much more preferably, methyl group.

In the case of a straight-chain or branched-chain alkyl group with from more than 6 carbon atoms, the polymerization reactivity of an obtained compound is lowered and it becomes difficult to obtain a polymer.

[0029]

The compound expressed by the above-mentioned general formula [1] includes, more preferably,

2-methyl-2,3-dihydrothieno [3, 4-b]-1,4-dioxin (2-methyl-EDOT)

2-ethyl-2,3-dihydrothieno [3, 4-b]-1,4-dioxin (2-ethyl-EDOT)

2-propyl-2,3-dihydrothieno [3, 4-b]-1,4-dioxin (2-propyl-EDOT)

2-isopropyl-2,3-dihydrothieno [3, 4-b]-1,4-dioxin (2-isopropyl-EDOT)

2-butyl-2,3-dihydrothieno [3, 4-b]-1,4-dioxin (2-butyl-EDOT)

2-pentyl-2,3-dihydrothieno [3, 4-b]-1,4-dioxin (2-pentyl-EDOT)

2-hexyl-2,3-dihydrothieno [3, 4-b]-1,4-dioxin (2-hexyl-EDOT) and the like.

[0030]

Polymer obtained by polymerizing a compound expressed by the above-mentioned general formula [1] shows high conductivity and is excellent in heat stability.

The above-mentioned compound used in the present invention is such that the polymerization rate is improved as compared with the well-known conductive polymer monomer, or for example, EDOT.

That is, although the polymerization rate is slower than that of EDOT, it shows excellent polymerization and therefore, the polymerization can be made up to the back of the pores in the valve-action

metal having porous complicated shape.

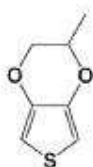
Hence, the polymer of the compound used in the present invention is a conductive polymer material suitable for a solid electrolyte of a solid electrolytic capacitor.

[0031]

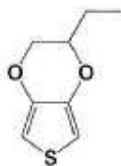
In the above-mentioned compound, when a compound expressed by at least one of the following formulas [2] and [3] is used, it is possible to obtain a solid electrolytic capacitor that is especially excellent in ESR characteristics and heat resistance.

[0032]

{ 2 }



{ 3 }



[0033]

The polymer obtained by polymerization of at least one of compounds expressed by the above-mentioned formulas [1] to [3] can be obtained by the following polymerization method.

For example, the polymer can be obtained by chemical oxidative polymerization of the above-mentioned compound with use of oxidant or by electro-chemical oxidative polymerization.

[0034]

The above-mentioned oxidant used in the chemical oxidative polymerization includes

halide such as iodine, bromine, bromine iodide, chlorine dioxide, iodic acid, periodic acid, and chlorous acid,

metal halide such as antimony pentafluoride, phosphorus pentachloride, phosphorus pentafluoride, aluminium chloride, and molybdenum chloride,

higher oxidation state transition metal ion such as permanganate, dichromate, chromic anhydride, cupric salt and its salt;

protonic acid such as trifluoromethanesulfonic acid, sulfuric acid and nitric acid;

oxygen compound such as liquid dioxide and sulfur trioxide; peroxy acid and salt such as sodium perborate, ammonium persulfate, hydrogen peroxide; and

heteropoly acid and salt such as tungstomolybdophosphoric acid, tungstophosphoric acid and molybdophosphoric acid.

[0035]

Besides, the electro-chemical oxidative polymerization may be made by electrolytic oxidation of dopant and at least one of compounds expressed by the above-mentioned formulas [1] to [3] in an electrolytic solution formed by dissolving in solvent.

[0036]

The above-mentioned dopants include, for example,

halogen ion such as chlorine, bromine iodine and halide ion such as perchloric acid, tetrafluoroboron, hexafluoroantimonate, hexafluoroarsine, hexafluoro phosphorus,

alkyl substituted organic sulfonic acid ion such as dodecylsulfonic acid, methanesulfonic acid,

circular sulfonic acid ion such as camphorsulfonic acid ion, alkyl substituted or unsubstituted benzene or disulfonic acid ion such as benzenedisulfonic acid, dodecylbenzenesulfonic acid, p-toluenesulfonic acid and benzenesulfonic acid,

alkyl substituted or unsubstituted ion of naphthalenesulfonic acid with one to four sulfonic acid substituted such as 2-naphthalenesulfonic acid, 1,7-naphthalenedisulfonic acid, anthracenesulfonic acid ion, anthracenequinonesulfonic acid ion,

alkyl substituted or unsubstituted biphenylsulfonic acid ion such as biphenyldisulfonic acid, alkylbiphenylsulfonic acid,

polymeric sulfonic acid ion such as naphthalenesulfonate formaldehyde condensate and polystyrenesulfonic acid,

heteropoly acid ion such as tungstomolybdophosphoric acid, tungstophosphoric acid and molybdophosphoric acid. These various salts can be used as a supporting electrolyte.

[0037]

Such solvents mentioned above include:

water,

ethers such as diethylether, dioxane, and tetrahydrofuran (THF),

ketones such as methyl ethyl ketone and acetone,

aprotic solvent such as diethyl carbonate (DEC), dimethyl carbonate (DMC), ethylene carbonate (EC), propylene carbonate (PC), γ -butyrolactone (GBL), dimethyl sulfoxide (DMSO), N-methylpyrrolidone (NMP), benzonitrile, acetonitrile, dimethylformamide (DMF),

esters such as butyl acetate and ethyl acetate,

nonaromatic chloride type solvent such as dichloromethane and chloroform,

nitro compound type solvent such as nitrobenzene, nitroethane, nitromethane,

alcohols such as ethylene glycol, butanol, isopropanol, propanol, ethanol and methanol,

organic acid such as propionic acid, acetic acid, formic acid and acid anhydride (acetic anhydride etc.) of the organic acid.

Needless to say, each of these solvents may be used alone, or any of them may be used in combination.

[0038]

the electro-chemical oxidative polymerization may be made by electrolytic oxidation of the above-mentioned compound in the above-mentioned electrolytic solution to form polymer on anode.

[0039]

The solid electrolytic capacitor of the present invention has a solid electrolyte layer containing molecules obtained by polymerization of at least one of compounds expressed by the formulas [1] to [3] and shows excellent electric properties, showing a high capacitance and a low ESR.

In addition, it shows significantly improved heat resistance compared with the conventional solid electrolytic capacitor of which the solid electrolyte layer is Poly-3,4-ethylenedioxythiophene (hereinafter abbreviated to "PEDOT")

[0040]

The solid electrolytic capacitor of the present invention shows lower ESR, which may be because the polymerization rate of the compound used in the present invention is relatively slower and the polymerization is allowed even after polymerization reaction solution penetrates well into a dielectric oxide film. Therefore, it is possible to form a solid electrolyte layer with good adhesion.

Further, the obtained molecules have a short-chain alkyl group as substituent, which causes an inductive effect, the electron distribution is wider than that of PEDOT (conjugated system is expanded) and as a result, conductivity is expected to be enhanced.

[0041]

Next description is made about a method for producing a solid electrolytic capacitor of the present invention.

The method for producing a solid electrolytic capacitor of the present invention is characterized by comprising a step of forming the molecules obtained by polymerization of a compound expressed by the above-mentioned formula [1] on a valve-action metal on which a dielectric oxide film has been formed

[0042]

The valve-action metal used here may be, for example, aluminum, tantalum, titanium, niobium or an alloy thereof. More preferably, the valve-action metal may be aluminum, tantalum or niobium.

Such valve-action metal may be preferably used in the form of metal foil, sintered powder or the like.

[0043]

The dielectric oxide film may be formed on the surface of the above-mentioned valve-action metal by performing anodic oxidation in a chemical solution such as diammonium adipate solution.

[0044]

The above-mentioned polymer may be formed by either of the above-mentioned chemical oxidative polymerization and electro-oxidative polymerization.

The chemical oxidative polymerization is more preferable in view of electric characteristics of the obtained solid electrolytic capacitor and simpler manufacturing process.

[0045]

The method for producing polymers on the valve-action metal by the chemical oxidative polymerization includes a step of bringing at least one (A) of compounds expressed by (1) to (3) mentioned above, a dopant (B) and an oxidant (C) into contact with each other in the liquid phase.

[0046]

The above-mentioned compound (A), dopant (B) and oxidant (C) may be brought into contact with each other in the liquid phase by the following methods:

1. A compound (A) expressed by at least one of the above-mentioned [1] to [3], dopant (B) and oxidant (C) are mixed to prepare a solution and the solution is brought into contact with a valve-action metal by impregnation or coating thereby to obtain molecules,

2. The above-mentioned compound is prepared, a solution containing dopant and oxidant is prepared separately, valve-action metal impregnated with the above-mentioned compound solution is coated or impregnated in the above-mentioned oxidant solution thereby to obtain molecules, and

3. A valve-action metal is coated or impregnated with a solution containing dopant and oxidant, impregnated with the above-mentioned compound solution and brought into contact therewith thereby to obtain molecules.

These methods are not intended for limiting the present invention.

[0047]

The molecules are formed on the valve-action metal by keeping a solution containing the compound (A), dopant (B) and oxidant (C) on the valve-action metal at predetermined temperatures and for a predetermined time period.

Here, the predetermined temperature can be freely selected from a range from 0 to 150 degrees, and the predetermined time can be freely selected from a range from 1 minute to 24 hours.

[0048]

As a preferable embodiment of the method for producing a solid electrolytic capacitor of the present invention, there is proposed a method of using a solution of a compound having both properties of dopant (B) and oxidant (C).

[0049]

The compound having both properties of dopant (B) and oxidant (C) is an oxidant containing an anion component as dopant of conductive polymer. With use of such an oxidant containing an anion component as dopant of conductive polymer, in chemical polymerization, the anion component can be taken in the conductive polymer to function as dopant, thereby enabling to obtain the conductive polymer with improved conductivity.

[0050]

The preferable anion component includes organic acid ions such as carboxylic acid ion and organic sulfonic acid ion, and inorganic acid ions such as boron compound ion and perchloric acid ion.

[0051]

The particularly preferable oxidant containing such an anion component includes inorganic acid iron(III) salt such as Iron(III) chloride and IRON(III) perchlorate and organic acid iron(III) salt such as benzenesulfonic acid iron(III), p-toluenesulfonate iron(III) salt and alkyl naphthalenesulfonate iron(III) salt. The most preferable one is organic sulfonic acid iron(III) salt.

[0052]

A solvent for dissolving a compound that contains properties

of both the dopant (B) and oxidant (C) includes alcohol type solvent such as methanol, ethanol, n-propanol, iso-propanol, n-butanol and ethylene glycol. Preferably, the solvent is ethanol or n-butanol.

[0053]

Most preferable one among them is the alcohol type solvent in which the above-mentioned organic sulfonic acid iron (III) is solved at a concentration ranging from 20% to 90% by weight mass percent, preferably at a concentration ranging from 30% to 80% by weight mass percent, or more preferably at a concentration ranging from 40% to 70% by weight mass percent.

With use of dopant (B) and oxidant dissolved at such a concentration, it is possible to form molecules that are excellent in conductivity and endurance on the complex shaped-valve-action metal in a dense manner.

[0054]

Next description is made about the method for producing the solid electrolytic capacitor of the present invention, by way of specific example of a method of producing an aluminum wound capacitor.

[0055]

First, a surface of anode aluminum foil is roughened by etching, and an anode lead is connected. Then, it is subjected to chemical conversion in a water solution such as Diammonium adipate or the like to form a dielectric oxide film. In carrying out the present invention, it is preferable that foil of larger etching magnification so as to be able to obtain a capacitor of larger capacitance.

[0056]

Separately between an opposed cathode aluminum foil with a cathode lead connected and the above-mentioned anode aluminum foil, a separator of Manila paper is provided to wind up it into a cylindrical

form, carbonize the separator by heat treatment thereby to prepare a wound type capacitor element.

[0057]

Then, a solid electrolyte layer made of conductive polymer is formed on the above-mentioned capacitor anode foil. This method for forming the solid electrolyte layer is of impregnating a capacitor element with a solution containing a compound of conductive polymer monomer expressed by at least one of the formulas [1] to [3] by immersion, coating, spraying or other method. The impregnated compound is then subjected to polymerization by contact with an oxidant thereby to form the solid electrolyte layer.

[0058]

Here, this process may be performed by impregnating the oxidant and bringing the above-mentioned compound into contact for polymerization or by impregnating with a solution containing a mixture of the above-mentioned compound and the oxidant together for polymerization. This method is not intended for limiting the present invention.

[0059]

Further, chemical oxidative polymerization is preferably performed by placing the oxidant, dopant and compound in contact in the liquid phase under temperatures of 0 to 150 degrees for a predetermined time period and drying the solvent by heating. When the temperature is lower than 0 degree, polymerization reaction is difficult to occur and when the temperature is higher than 150 degrees, capacitor performance may be deteriorated.

[0060]

The impregnating and heating steps mentioned above may be repeated plural times.

[0061]

With these steps, it is possible to form the solid electrolyte layer in which fine etching pits of anode aluminum foil are filled with conductive polymer layer.

[0062]

Then, the epoxy resin is used to seal the capacitor case, and voltage is applied to conduct aging so that the solid electrolytic capacitor of the present invention can be obtained.

[0063]

Hereinafter, the present invention will be described in detail based on examples, which however are not intended for limiting the present invention.

Here, in the examples, "%" represents "percent by mass". And, the capacitance (C) and dielectric loss ($\tan\delta$) are measured at a frequency of 120 Hz and the ESR (Equivalent Series Resistance) is measured at a frequency of 100 kHz except for the case specified particularly.

Besides, the impregnation rate is a percentage of the capacitance of the obtained solid electrolytic capacitor to a capacitance obtained by measuring the capacitor element before forming of the solid electrolyte layer in the 15% diammonium adipate solution.

Further, LC represents leakage current, which is a value of direct current in the solid electrolytic capacitor measured 60 seconds after rated voltage is applied.

Furthermore, the withstand voltage is a voltage (V) measured when the direct current flowing in the solid electrolytic capacitor exceeds 200 mA after the voltage is applied to both ends of the solid electrolytic capacitor. Here, the voltage is applied in such a manner that 15V is first applied and the voltage is increased by 1V every

30 seconds to monitor the direct current flow in the solid electrolytic capacitor.

Example 1

[0064]

[Method for producing a solid electrolytic capacitor with use of 2-methyl-2,3-dihydrothieno [3, 4-b]-1,4-dioxin (2- methyl-EDOT)]

The surface of aluminum foil is etched to be roughened and the anode lead is connected by caulking. Then, in the 10% diammonium adipate solution, the chemical conversion treatment is performed at a voltage of 4V so that a dielectric oxide film is formed on the surface of the aluminum foil.

[0065]

Then, Manila paper having a thickness of 50 μm is sandwiched as a separator between the above-mentioned anode foil and the facing cathode aluminum foil connected with the cathode lead by resistance welding, wound in a cylindrical form, and then subjected to heat treatment at a temperature of 400 degrees for four minutes to carbonize the Manila paper so that the capacitor element is prepared. The capacitance of the obtained capacitor element in the 15% diammonium adipate is 650 μF .

[0066]

Next, a compound to be used for polymerization, that is, 2-methyl-2,3-dihydrothieno [3, 4-b]-1,4-dioxin (2- methyl-EDOT), and an oxidant "Iron(III) p-toluenesulfonate 50% n-butanol solution" are prepared at a weight rate of 1 to 2.5. The capacitor element is impregnated in this solution for 120 seconds, heated at a temperature of 45 degrees for 2 hours, heated at a temperature of 105 degrees for 35 minutes, and heated at a temperature of 125 degrees for 1 hour

to conduct chemical oxidative polymerization. Then, the poly-2-methyl-EDOT is formed in the capacitor element.

[0067]

Then, epoxy resin is used to seal this capacitor case and voltages 4V is applied to both poles to perform aging thereby completing a solid electrolytic capacitor.

Example 2

[0068]

[Method for producing a solid electrolytic capacitor with use of 2-ethyl-2,3-dihydrothieno [3, 4-b]-1,4-dioxin (2- ethyl-EDOT)]

[0069]

The preprocessed capacitor like in Example 1 was prepared and the same method as Example 1 was performed except for the compound used in polymerization which was changed from 2-methyl-2,3-dihydrothieno [3, 4-b]-1,4-dioxin (2- methyl-EDOT) used in Example 1 to 2-ethyl-2,3-dihydrothieno [3, 4-b]-1,4-dioxin (2-ethyl-EDOT) thereby to produce the solid electrolytic capacitor.

Example 3

[0070]

[Method for producing a solid electrolytic capacitor with use of 2-propyl-2,3-dihydrothieno [3, 4-b]-1,4-dioxin (2- propyl-EDOT)]

[0071]

The preprocessed capacitor like in Example 1 was prepared and the same method as Example 1 was performed except for the compound used in polymerization which was changed from 2-methyl-2,3-dihydrothieno [3, 4-b]-1,4-dioxin (2- methyl-EDOT) used in Example 1 to 2-propyl-2,3-dihydrothieno [3, 4-b]-1,4-dioxin

(2-propyl-EDOT) thereby to produce the solid electrolytic capacitor.

[0072]

[Comparative Example 1]

[Method for producing a solid electrolytic capacitor with use of 2,3-dihydrothieno [3, 4-b]-1,4-dioxin (EDOT)]

The preprocessed capacitor like in Example 1 was prepared and the same method as Example 1 was performed except for the compound used in polymerization which was changed from 2-methyl-2,3-dihydrothieno [3, 4-b]-1,4-dioxin (2-methyl-EDOT) used in Example 1 to 2,3-dihydrothieno [3, 4-b]-1,4-dioxin (EDOT) thereby to produce the solid electrolytic capacitor.

Table 1 shows initial electric properties, capacitance impregnation rate and electric properties of leakage current and withstand voltage of the solid electrolytic capacitors obtained in Examples 1 to 3 and Comparative Example 1.

[0073]

Table 1

		Initial electric property			Capacitance Impregnation rate (%)	LC/ μ A 4V-60s	Withstand voltage (V)
		C(μ F)	$\tan \delta$ (%)	ESR(m Ω)			
Example 1	Methyl EDOT	569	3.8	7.9	87.5	9400	26
Example 2	Ethyl EDOT	561	4.9	9.8	86.3	2600	35
Example 3	Propyl EDOT	544	4.5	14.4	83.7	1800	43
Comparative Example 1	EDOT	574	4.8	12.5	88.3	4100	21

[0074]

As seen in Table 1, comparison of the various compounds results in that the solid electrolytic capacitors obtained in Examples 1 to 3 have lower Equivalent Series Resistance values than the solid electrolytic capacitor using EDOT in Comparative Example.

Particularly, it is evident that the ESR value of the solid electrolytic capacitor obtained in the example 1 is significantly reduced.

Example 4

[0075]

Iron(III) p-toluenesulfonate 50% n-butanol solution was prepared 0.3 g as oxidant on a 6ml vial and maintained at 20 C° for 30 minutes.

Next, a compound used for polymerization, that is, 0.1 g 2-methyl-2,3-dihydrothieno [3, 4-b]-1,4-dioxin (2- methyl-EDOT) was added to the vial and measurement started.

5 seconds later after addition, content in the vial was stirred vigorously for 10 seconds by a spatula.

Then, measurement was made of a time period from the time when stirring was finished to the time when a solid started to be precipitated in the vial. Results of this measurement were shown in Table 2.

Here, the polymerization rate in Table 2 is a value obtained by subtracting 10 seconds from seconds taken for precipitation of the solid.

Example 5

[0076]

The experiment was performed in the same manner as in Example

4, except for 2-ethyl-2,3-dihydrothieno [3, 4-b]-1,4-dioxin (2-ethyl-EDOT) which was used instead of 2-methyl-2,3-dihydrothieno [3, 4-b]-1,4-dioxin (2-methyl-EDOT) of Example 4. Experimental results are shown in Table 2.

Example 6

[0077]

The experiment was performed in the same manner as in Example 4, except for 2-propyl-2,3-dihydrothieno [3, 4-b]-1,4-dioxin (2-propyl-EDOT) which was used instead of 2-methyl-2,3-dihydrothieno [3, 4-b]-1,4-dioxin (2-methyl-EDOT) of Example 4. Experimental results are shown in Table 2.

[0078]

[Comparative Example 2]

The experiment was performed in the same manner as in Example 4, except for 2-hexyl-2,3-dihydrothieno [3, 4-b]-1,4-dioxin (2-hexyl-EDOT) which was used instead of 2-methyl-2,3-dihydrothieno [3, 4-b]-1,4-dioxin (2-methyl-EDOT) of Example 4. During measuring the polymerization rate, no solid matter could be found participated. The viscosity of the content was increased with time and the content became tarry. The time when the liquid flow was stopped is shown in Table 2.

[0079]

[Comparative Example 3]

The experiment was performed in the same manner as in Example 4, except for 2,3-dihydrothieno [3, 4-b]-1,4-dioxin (EDOT) which was used instead of 2-methyl-2,3-dihydrothieno [3, 4-b]-1,4-dioxin (2-methyl-EDOT) of Example 4. Experimental results are shown in Table 2.

[0080]

Table 2

		Polymerization rate (second)
Example 4	Methyl EDOT	103
Example 5	Ethyl EDOT	208
Example 6	Propyl EDOT	370
Comparative Example 2	Hexyl EDOT	804
Comparative Example 3	EDOT	69

[0081]

The results of Examples 4 to 6 and Comparative Examples 1 and 2 are shown in a graph of Fig. 1, in which the horizontal axis indicates the carbon numbers of the methyl group, ethyl group, propyl group and hexyl group as substituent of EDOT and the vertical axis indicates the polymerization rates (seconds).

As seen from Fig. 1, the polymerization rate is much lowered when the alkyl group with 3 or more carbon atoms is substituted for EDOT.

Example 7

[0082]

In the condition of Example 1 and the humidity of 22 %, 2-methyl-2,3-dihydrothieno [3, 4-b]-1,4-dioxin (2- methyl-EDOT) 1.10 g and Iron(III) p-toluenesulfonate 50%/n-butanol solution as oxidant were prepared at a weight ratio of 1:2:5 and stirred 60 seconds.

Then, the capacitor element used in Example 1 was impregnated in this solution 120 seconds, which was then put in a closed bottle in a glove box. 30 minutes later, it was heated 45 C° for 2 hours, and the capacitor element was taken out of the closed bottle and heated 105 C° for 35 minutes and 125 C° for 1 hour. After that, the chemical

oxidative polymerization was conducted to form poly-2-methyl-EDOT in the capacitor element.

Example 8

[0083]

The processing was performed in the same manner as in Example 7, except for 2-ethyl-2,3-dihydrothieno [3, 4-b]-1,4-dioxin (2-ethyl-EDOT) which was used instead of 2-methyl-2,3-dihydrothieno [3, 4-b]-1,4-dioxin (2-methyl-EDOT) of Example 7 to produce a solid electrolytic capacitor. Results are shown in Table 3.

Example 9

[0084]

The processing was performed in the same manner as in Example 7, except for 2-propyl-2,3-dihydrothieno [3, 4-b]-1,4-dioxin (2-propyl-EDOT) which was used instead of 2-methyl-2,3-dihydrothieno [3, 4-b]-1,4-dioxin (2-methyl-EDOT) of Example 7 to produce a solid electrolytic capacitor. Results are shown in Table 3.

[0085]

[Comparative Example 4]

The processing was performed in the same manner as in Example 7, except for 2-hexyl-2,3-dihydrothieno [3, 4-b]-1,4-dioxin (2-hexyl-EDOT) which was used instead of 2-methyl-2,3-dihydrothieno [3, 4-b]-1,4-dioxin (2-methyl-EDOT) of Example 7 to produce a solid electrolytic capacitor. Results are shown in Table 3.

[0086]

[Comparative Example 5]

The processing was performed in the same manner as in Example 7, except for 2,3-dihydrothieno [3, 4-b]-2-hydroxymethyl-1,4-dioxin

(2-hydroxymethyl-EDOT) which was used instead of 2-methyl-2,3-dihydrothieno [3, 4-b]-1,4-dioxin (2-methyl-EDOT) of Example 7 to produce a solid electrolytic capacitor. Results are shown in Table 3.

[0087]

[Comparative Example 6]

The processing was performed in the same manner as in Example 7, except for 2-methyl-2,3-dihydrothieno [3, 4-b]-1,4-dioxin (2-methyl-PDOT) which was used instead of 2-methyl-2,3-dihydrothieno [3, 4-b]-1,4-dioxin (2-methyl-EDOT) of Example 7 to produce a solid electrolytic capacitor. However, sufficient performance could not be achieved in the produced solid electrolytic capacitor.

[0088]

[Comparative Example 7]

The processing was performed in the same manner as in Example 7, except for 2,3-dihydrothieno [3, 4-b]-1,4-dioxin (EDOT) which was used instead of 2-methyl-2,3-dihydrothieno [3, 4-b]-1,4-dioxin (2-methyl-EDOT) of Example 7 to produce a solid electrolytic capacitor. Results are shown in Table 3.

[0089]

Then, the solid electrolytic capacitors obtained in Examples 7 to 9 and Comparative Examples 4 to 7 were subjected to a heat test on the conditions of the temperature 125 C° and applied voltage 4.0 V. Test data of before the heat test, 24-hour later, 48-hour later and 1000-hour later are shown in Table 3.

[0090]

Table 3

		C (μF)				tanδ(%)				ESR(mΩ)				LCi(AV40s)			
		Initial	24h	48h	1000h	Initial	24h	48h	1000h	Initial	24h	48h	1000h	Initial	24h	48h	1000h
Example 7	Me-EDOT	569	589	585	538	3.8	4.8	5.1	8.4	7.9	8.5	9.3	25.2	9400	2700	100	30
Example 8	Et-EDOT	561	582	569	527	4.9	5.8	6.6	8.9	9.8	10.8	11.8	31.7	2600	600	5	2
Example 9	Pr-EDOT	544	569	551	503	4.5	5.7	6.9	15.3	14.4	18.1	22.4	53.2	1800	6	3	1
Comparative Example 4	Hex-EDOT	562	550	507	402	11.9	16.1	20.0	43.8	27.0	43.0	62.8	180.5	450	2	3	1
Comparative Example 5	CH ₂ OH-EDOT	521	513	474	331	24.8	24.8	27.1	50.3	72.6	88.1	110.1	450.5	260	6	4	1
Comparative Example 7	EDOT	574	584	583	519	4.8	5.4	6.3	13.9	12.5	14.3	16.2	46.9	4100	1500	300	50

[0091]

The results of Examples 7 to 9 and Comparative Examples 4 and 7 are shown in a graph of Fig. 2, in which the horizontal axis indicates the carbon numbers of the methyl group, ethyl group, propyl group and hexyl group as substituent of EDOT and the vertical axis indicates ESR (mΩ).

As seen from Fig. 2, when the alkyl group with 1 or 2 carbon

atoms is substituted for EDOT, the ESR becomes small. Particularly when the alkyl group with 1 carbon atom is substituted for EDOT, the ESR becomes smaller.

[0092]

[Reference Example]

A tantalum sintered body of $5 \times 3 \times 1 \text{ mm}^3$ size was used as anode and the anode body using a tantalum ray as anode ray and having a weight of about 100 mg was subjected to anodic oxidation in 0.05 weight% phosphoric acid solution at a temperature of 80 C° and 25 V for 150 minutes. Then, it was cleaned by running deionized water and dried to be a capacitor element. Here, this state was regarded as a capacitor and capacitance in the chemical solution was measured, which result was 160 μF .

Example 10

[0093]

[Method for producing a solid electrolytic capacitor with use of 2-methyl-2,3-dihydrothieno [3, 4-b]-1,4-dioxin (2- methyl-EDOT)]

Fig. 3 is a schematic cross sectional view for explaining the structure of the solid electrolytic capacitor according to Example 10 of the present invention.

Tantalum metal particles were pressure-formed to be sintered anode 11, which was subjected to chemical conversion coating in the electrolysis solution of the phosphoric acid solution to form the capacitor element with dielectric oxide film 12 formed on the surface.

[0094]

Next, the above-mentioned capacitor element was impregnated in a chemical polymerization solution consisting of 2-methyl-2,3-dihydrothieno [3, 4-b]-1,4-dioxin (2- methyl-EDOT),

Iron(III) p-toluenesulfonate and butyl alcohol, and subjected to heat treatment in the atmosphere and solid electrolyte 13 consisting of poly(2-methyl-EDOT) was formed on the dielectric oxide film 12 by chemical oxidative polymerization. These immersion and heat treatment steps are repeated five times or more. This-time heat treatment was conducted in such a manner as to keep it at room temperatures for 10 minutes and then, 150 °C and for 5 minutes

[0095]

Then, a graphite layer 14 and a silver paste layer 15 were sequentially formed on the solid electrolyte layer 13 and a cathode lead 17 was connected to the silver paste layer 15 via a conductive adhesive agent 19 and the anode lead 16 was connected to the anode 11. They were molded by a resin outer sheath 18 and the solid electrolytic capacitor was completed.

Example 11

[0096]

[Method for producing a solid electrolytic capacitor with use of 2-ethyl-2,3-dihydrothieno [3, 4-b]-1,4-dioxin (2-ethyl-EDOT)]

A preprocessed capacitor element like in Example 1 was prepared and the processing was conducted in the same method as Example 10 except for 2-ethyl-2,3-dihydrothieno [3, 4-b]-1,4-dioxin (2-ethyl-EDOT) used as monomers thereby to produce a solid electrolytic capacitor.

Example 12

[0097]

[Method for producing a solid electrolytic capacitor with use of 2-propyl-2,3-dihydrothieno [3, 4-b]-1,4-dioxin (2-propyl-EDOT)]

A preprocessed capacitor element like in Example 1 was prepared and the processing was conducted in the same method as Example 10 except for 2-propyl-2,3-dihydrothieno [3, 4-b]-1,4-dioxin (2-propyl-EDOT) used as monomers thereby to produce a solid electrolytic capacitor.

[0098]

[Comparative Example 8]

[Method for producing a solid electrolytic capacitor with use of 2,3-dihydrothieno [3, 4-b]-1,4-dioxin (EDOT)]

A preprocessed capacitor element like in Example 9 was prepared and the processing was conducted in the same method as Example 1 except for 2,3-dihydrothieno [3, 4-b]-1,4-dioxin (2-propyl-EDOT) used as monomers thereby to produce a solid electrolytic capacitor.

[0099]

As to the solid electrolytic capacitors obtained in Examples 10 to 12 and Comparative Example 8, their initial electric properties and electric properties of impregnation rate are shown in Table 4.

[0100]

Table 4

	Initial electric property			Capacitance Impregnation rate (%)
	C (μ F)	$\tan \delta$ (%)	ESR(m Ω)	
Example 1	147	2.0	22.0	91.9
Example 2	145	2.5	23.3	90.6
Example 3	130	2.4	27.0	81.3
Comparative Example	135	2.5	25.6	84.4

[0101]

As shown in Table 1, it is clear from the comparison results of various monomer units, the solid electrolytic capacitors of the

present invention (Examples 9 to 12) have higher impregnation rates and lower ESR than the conventional solid electrolytic capacitors that uses EDOT.

[0102]

The present specification is based on Japanese Patent Applications No. 2009-252488 filed on November 2, 2009, the entire contents of which are expressly incorporated by reference herein.

INDUSTRIAL APPLICABILITY

[0103]

As the solid electrolytic capacitor of the present invention has higher capacitance, lower ESR and more excellent in heat resistance, it is broadly applicable to consumer or industrial electronics devices.

REFERENCE NUMERALS

[0104]

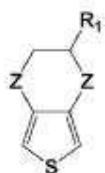
- 1... Comparative Example 3
- 2... Example 4
- 3... Example 5
- 4... Example 6
- 5... Comparative Example 2
- 6... Comparative Example 7
- 7... Example 7
- 8... Example 8
- 9... Example 9
- 10... Comparative Example 4
- 11... anode
- 12... dielectric oxide film
- 13... solid electrolyte

- 14... graphite layer
- 15... silver paste layer
- 16... anode lead
- 17... cathode lead
- 18... resin outer sheath
- 19... conductive adhesive

CLAIMS

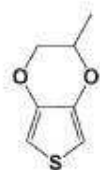
1. A solid electrolytic capacitor comprising, as solid electrolyte, molecules obtained by polymerizing a compound expressed by a formula [1] (in the formula, R₁ represents a straight-chain or branched-chain alkyl group with from 1 to 6 carbon atoms and Z represents oxygen atom or sulfur atom, independently).

[1]



2. A solid electrolytic capacitor comprising, as solid electrolyte, molecules obtained by polymerizing at least one of compounds expressed by formulas [2] and [3].

[2]



[3]



3. The solid electrolytic capacitor of claim 2, wherein the molecules are obtained by polymerizing the compound expressed by the formula [2].

4. The solid electrolytic capacitor of claim 2, further comprising:
 a porous body, as an anode, obtained by sintering valve-action metal particles;

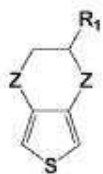
 a dielectric oxide film formed on a surface of the anode;

 solid electrolyte containing molecules obtained by polymerizing the compound expressed by at least one of the formulas [2] and [3] on a surface of the dielectric oxide film; and

 a cathode having a carbon layer and a silver layer formed on the molecules.

5. The solid electrolytic capacitor of claim 4, wherein the valve-action metal particles used in the porous body obtained by sintering of the valve-action metal particles contain at least one of tantalum metal particles and niobium metal particles, and a CV product per unit mass is 20000 $\mu\text{FV/g}$ or more.

6. A method for producing a solid electrolytic capacitor comprising a step of obtaining molecules by polymerizing a compound expressed by a formula [1] and forming the molecules on valve-action metal where a dielectric oxide film is formed (in the formula, R1 represents a straight-chain or branched-chain alkyl group with from 1 to 6 carbon atoms and Z represents oxygen atom or sulfur atom, independently).
 [1]



7. A method for producing a solid electrolytic capacitor comprising a step of obtaining molecules by polymerizing at least one of compounds expressed by formulas [2] and [3] and forming the molecules on valve-action metal where a dielectric oxide film is formed.

[2]



[3]



8. The method of claim 7, wherein the step of forming the molecules on the valve-action metal where the dielectric oxide film is formed comprises performing polymerization by bringing (A) at least one selected from a group consisting of compounds expressed by formulas [1] to [3], (B) a dopant, and (C) an oxidant into contact with each other in a liquid phase.

9. The method of claim 8, wherein (B) the dopant and (C) the oxidant are replaced with a compound having properties of both (B) the dopant and (C) the oxidant.

10. The method of claim 9, wherein the compound having properties of both (B) the dopant and (C) the oxidant is organic sulfonic acid iron(III) salt and the liquid phase contains 40 to 70 wt% of the organic sulfonic acid iron(III) salt.

11. The method of claim 7, wherein a porous body obtained by sintering valve-action metal particles is used as an anode and the method further comprises:

forming the dielectric oxide film on a surface of the anode;

forming the molecules obtained by polymerization of at least one of the compounds expressed by the formulas [2] and [3], on the anode where the dielectric oxide film is formed; and

forming a cathode containing a carbon layer and a silver layer on the molecules.

12. The method of claim 11, wherein the step of forming the molecules on the anode where the dielectric oxide film is formed comprises: bringing (A) the at least one selected from the group consisting of the compounds expressed by the formulas [1] to [3] and (C) the oxidant into contact with each other in the liquid phase to conduct chemical oxidative polymerization.