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TITLE OF THE INVENTION

SOLID ELECTROLYTIC CAPACITOR AND MANUFACTURING
METHOD THEREOF

5 BACKGROUND OF THE INVENTION

Field of the Invention

The present invention generally relates to a solid electrolytic capacitor, and more particularly to a method of manufacturing a solid electrolytic capacitor with a solid electrolyte layer which is commonly used in various electronic apparatuses.

Description of the Prior Art

A conventional method of manufacturing a solid electrolytic capacitor will be explained below with reference to relevant drawings.

Fig. 12 is a cross sectional view showing a construction of a conventional solid electrolytic capacitor. As shown in Fig. 12, denoted by reference numeral 20 is a porous anode element which is fabricated by press forming a valve action metal of tantalum powder into a desired shape and sintering the resultant shape. Reference numeral 21 denotes an anode lead line made of a tantalum line which is inserted into the anode element 20.

A dielectric oxide coating layer 22 is provided on an

outer surface of the anode element 20, a solid electrolyte layer 23 is provided on the dielectric oxide coating layer 22, and a cathode layer 24 is provided on the solid electrolyte layer 23. The cathode layer 24 is formed as a layer structure by laminating carbon and silver paint. Thus, a capacitor element 25 is fabricated. An anode terminal 26 is connected to the anode lead line 21 of the capacitor element 25, a cathode terminal 27 is bonded to the cathode layer 24 by an electrically conductive adhesive 28, and an resin enclosure 29 of commonly an epoxy resin material encapsulates the capacitor element 25 with the anode terminal 26 and cathode terminal 27 partially exposed to the outside. Reference numeral 30 denotes a resin reinforcement.

A method of manufacturing the conventional solid electrolytic capacitor will now be explained referring to Fig. 13. Fig. 13 illustrates a flowchart of steps for producing the conventional solid electrolytic capacitor. First, in a forming and sintering step S91, a metal powder of tantalum is press formed into a desired shape having the anode lead line 21 of tantalum line embedded therein and then sintered to form a porous anode element 20.

This is followed by a chemical processing step S92 for oxidizing the anode element 20 with phosphoric acid to

thereby form a dielectric oxide coating layer 22. Then, a polymerizing step S93 follows where the anode element 20 is subjected to uniform dispersion of a monomer solution including aniline, pyrrole, or thiophene over the outer
5 surface and in the pores thereof, and then exposed directly to a solution containing an oxidizer or subjected to uniform dispersion of the oxidizer, and then exposed directly to the monomer solution to thereby form a solid electrolyte layer 23 of an electrically conductive polymer
10 through chemical oxidation polymerization.

Then in a cathode forming step S94, a coating of carbon and a coating of silver paint are applied and drying is performed to thereby form a cathode layer 24. As a result, a capacitor element 25 is fabricated.

15 Then, the process proceeds to an assembling step S95, where the anode lead line 21 of the capacitor element 25 is joined by welding to an anode terminal 26 acting as a COM port, and the cathode layer 24 is bonded to a cathode terminal 27 through an electrically conductive adhesive 28.

20 A molding step S96 follows where the capacitor element 25 is encapsulated in a resin enclosure 29 of an epoxy resin material with the anode terminal 26 and cathode terminal 27 exposed partially to the outside. Finally, a finishing step S97 is carried out for separating a

capacitor array into chips which are then tested.

The solid electrolyte layer may be fabricated by another method such as disclosed in Japanese Patent Laid-open Publication 10-321474 where the solid electrolyte layer of a solid electrolytic capacitor consists mainly of a first solid electrolyte layer formed by heating a solution of poly-aniline or its derivative and a second solid electrolyte layer formed by electrolytically polymerizing poly-pyrrole or its derivative. As its resultant solid electrolyte layer is uniform in thickness, the solid electrolytic capacitor can be enhanced in static capacitance and its impedance characteristic, thus offering the solid electrolytic capacitor with a higher degree of reliability.

The conventional method of making a solid electrolytic capacitor, however, has a disadvantage in the polymerizing step S93 that during the formation of a solid electrolyte layer 23 of poly-pyrrole over the outer surface and in the pores of the anode element 20 through repeating a chemical oxidation polymerization process, residues 31 of the electrically conductive polymer are substantially deposited on the outer surface and in the pores of the anode element 20 as shown in Figs. 14 and 15.

The electrically conductive polymer residues 31

include byproducts of the chemical oxidation polymerization and non-reacted portions of the electrically conductive polymer or the oxidizer, which may impair the appearance and decline the volumetric compactness and the other characteristics of the capacitor element 25. In a worse case, the residues 31 may be exposed on the resin enclosure 29. It is hence necessary to remove the residues 31 with use of a brush or broom in order to smooth the surface of the solid electrolyte layer 23 and correct the appearance before the cathode layer forming step S94. As a result, the productivity will be declined. Also, if the removal of the residues 31 is improperly conducted, the electrically conductive polymer layer 23 may be injured thus impairing the characteristics of the capacitor.

15 In the polymerizing step S93, the anode element 20 is immersed in one of the two solutions containing the monomer and the oxidizer respectively and is then immersed in the other. This causes one of the two solutions to be carried and dispersed into the other as the anode element 20 is immersed. As the other solution is declined in concentration, the formation of an electrically conductive polymer in the anode element 20 is disturbed. Accordingly, the solid electrolyte layer 23 of continuous electrically conductive polymer will hardly be formed on the dielectric

oxide coating layer 22. Hence, the static capacitance and impedance characteristics are deteriorated.

It is needed for coating the dielectric oxide coating layer 22 of the anode element 20 with the solid electrolyte layer 23 of electrically conductive polymer so that the solid electrolytic capacitor can hold a designed level of capacitance. Also, in order to attain a good (i.e., low) impedance characteristic, it is necessary to repeat the step of forming the solid electrolyte layer 23 of electrically conductive polymer several times. As a result, the productivity is declined to be a problem.

Also, the technology disclosed in Japanese Patent Laid-open Publication 10-321474 includes a step of forming the first solid electrolyte layer by heating a solution where polymeric aniline or its derivative is dissolved into a water-contained solvent. This, however, causes the first solid electrolyte layer to be dissolved partially during the succeeding step of forming the second solid electrolyte layer. Hence, it is difficult to enhance the static capacitance.

It is therefore an object of the present invention to provide a solid electrolytic capacitor and a method of manufacturing a solid electrolytic capacitor which eliminates the foregoing problems and is stable and high in

the productivity so that products thereof are increased in static capacitance and improved in reliability.

SUMMARY OF THE INVENTION

5 The present invention has been developed to solve these problems inherent to the conventional techniques, and an essential object of the present invention is to provide an improvement of a method of manufacturing a solid electrolytic capacitor

10 According to a first aspect of the present invention, a method of manufacturing a solid electrolytic capacitor includes the steps of: providing a dielectric oxide film on a surface of an anode element made of a valve metal; immersing the anode element into a water solution of
15 electrically conductive polymer containing a hydrophilic group in a polymer structure and then drawing up the anode element and heating the same to form an electrically conductive polymer layer on the dielectric oxide cladding layer; coating the electrically conductive polymer layer
20 with a solution containing a monomer of a heterocyclic compound or its derivative, and polymerizing the monomer in the solution to form a polymer layer, rinsing the anode element to remove residues deposited on the polymer layer, and drying the anode element to form a first solid

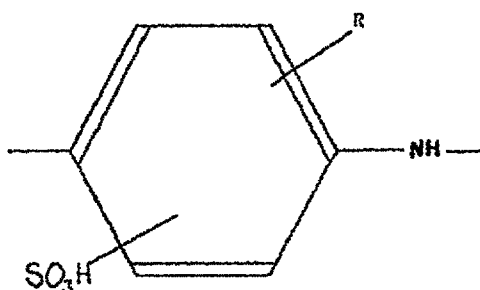
electrolyte layer; and providing a cathode layer on the first solid electrolyte layer.

This allows the production of a solid electrolytic capacitor to be improved in the efficiency and the low
5 impedance characteristic, declined in the leak current, and increased in the static capacitance while being carried out stably.

The electrically conductive polymer having a hydrophilic group in the polymer structure may be a
10 derivative of aniline, pyrrole, thiophene, or furan of the monomer.

This allows its solid electrolytic capacitor to be improved in the electrical conductivity and the impedance characteristic at a higher frequency range.

15 The electrically conductive polymer having a hydrophilic group in the polymer structure may be a self-doping type electrically conductive polymer having a sulfonic group. The electrically conductive polymer having a hydrophilic group in the polymer structure may be an
20 aniline derivative expressed by Formula 1,
(Formula 1)



where R in Formula 1 is selected from hydrogen, alkyl groups, alkoxy groups, hydroxyl groups, and nitro groups.

Those simple techniques allow their solid electrolytic
5 capacitor to be improved in the impedance characteristic at a higher frequency range and the withstand voltage and declined in the current leakage.

The water solution of the electrically conductive polymer having a hydrophilic group in the polymer structure
10 may have a surface tension of not higher than 70×10^{-3} N/m.

This allows the dielectric oxide coating layer to be improved in the permeability. If the surface tension of the water solution exceeds 70 mN/m, the permeability of the dielectric oxide coating layer may unfortunately be
15 declined.

The heating may be conducted at a temperature ranging from 160 to 250 °C. This allows the hydrophilic group in the electrically conductive polymer layer to be partially decomposed thus declining the dissolution.

20 If the temperature for the heating is lower than 160

°C, the dissolution of the electrically conductive polymer layer into water will be increased thus failing to improve the static capacitance and the withstand voltage. Also, if the temperature exceeds 250 °C, the electrically conductive polymer layer will receive more thermal stress hence increasing the current leakage.

The formation of the first solid electrolyte layer may be implemented by a chemical oxidation polymerization process using an oxidizer. The step of providing the first solid electrolyte layer may be implemented by repeating at least two or more times a procedure of: immersing the anode element into one of a monomer solution and an oxidizing solution for a predetermined time and then into the other solution for a predetermined time to form a polymer layer and subsequently restoring the dielectric oxide cladding layer. The temperature of the oxidizing solution may be lower than that when holding in the air.

Those features allow the solid electrolyte layer to be highly improved in the electrical conductivity.

The step of providing the first solid electrolyte layer may be implemented by electrolytic polymerization. The electrolytic polymerization may be performed using a water solution of pH not greater than pH 5 which contains at least a monomer of a heterocyclic compound or its

derivative, a pH adjustment agent and water.

By this method, the polymerization speed is improved. Also, even in the case where a capacitor is left in an initial and high temperature conditions, a solid electrolytic capacitor can be improved in low impedance characteristic.

The rinsing for removing residues may be implemented by removing the residues at least either from the outer surface of the anode element or from the pores in the anode element. The rinsing for removing residues either from the outer surface of the anode element or the pores in the anode element may be implemented by rinsing with a shower of liquid including water, hot water, or organic solvent or air or gas, by ultrasonic rinsing, or by blasting.

Those features can elevate the effect of highly improving the electrical conductivity while declining the current leakage on the solid electrolyte layer.

The step of providing the first solid electrolyte layer may be followed by a step of providing a second solid electrolyte layer under a different condition from that of providing the first solid electrolyte layer.

This allows the solid electrolyte layer to be declined in the current leakage and improved in the electrical conductivity.

The step of providing the first solid electrolyte layer may be followed by a step of providing a second solid electrolyte layer under a different condition from that of providing the first solid electrolyte layer and then
5 followed by a step of providing a third solid electrolyte layer of an electrically conductive polymer different from the first and second solid electrolyte layers.

The step of providing the third solid electrolyte layer may be implemented by repeating at least one or more
10 times a procedure of immersing the anode element into a suspension containing a monomer, an oxidizer, and an electrically conductive polymer in particle form for a predetermined time and after drawing up from the suspension, holding the same outside the suspension for a predetermined
15 time.

The suspension may be prepared by mixing a predetermined amount of monomer and a predetermined amount of oxidizer to form electrically conductive polymer particles and adding the monomer.

20 Those allow the solid electrolyte layer to be effectively declined in the current leakage and improved in the electrical conductivity.

The step of providing the third solid electrolyte layer may be implemented by electrolytic polymerization.

The electrolytic polymerization is performed using a water solution of pH not greater than pH 5 which contains at least a monomer of a heterocyclic compound or its derivative, a pH adjustment agent and water.

5 By this method, the polymerization speed is improved. Also, even in the case where a capacitor is left in an initial and high temperature conditions, a solid electrolytic capacitor can be improved in low impedance characteristic.

10 The step of providing the first solid electrolyte layer may include restoring the dielectric oxide film prior to the rinsing of the polymer film for removing the residues. This can minimize the current leakage.

 The step of providing the cathode layer may be
15 followed by heating again. The heating is conducted at a temperature ranging from 230 to 280 °C. Those features can improve the bonding strength between the solid electrolyte layer and the cathode layer thus enhancing the low impedance characteristic and declining the current leakage.

20 According to a second aspect of the present invention, a solid electrolytic capacitor is fabricated by any one of the solid electrolytic capacitor manufacturing methods described above. The residues deposited on the electrically conductive polymer layer may be smaller than

5 % by weight.

Those features can improve the low impedance characteristic, decline the current leakage, and increase the static capacitance while allowing the production to be
5 stable.

BRIEF DESCRIPTION OF THE DRAWINGS

These and other objects and features of the present invention will be readily understood from the following
10 detailed description taken in conjunction with preferred embodiments thereof with reference to the accompanying drawings, in which like parts are designated by like reference numerals and in which:.

Fig. 1 is a flowchart showing steps of a solid
15 electrolytic capacitor manufacturing method according to Embodiment 1 of the present invention;

Fig. 2 is a front cross sectional view of a rinsing apparatus according to Embodiment 2 of the present invention;

20 Fig. 3 is a front view of a capacitor element after the rinsing with a shower according to the embodiment;

Fig. 4 is a cross sectional view showing the pores in an anode body after the rinsing with a shower according to Embodiment 3 of the present invention;

Fig. 5 is a flowchart showing steps of a solid electrolytic capacitor manufacturing method according to Embodiment 4 of the present invention;

Fig. 6 is a flowchart showing steps of a solid electrolytic capacitor manufacturing method according to Embodiment 6 of the present invention;

Fig. 7 is a characteristic graph view of a solid electrolytic capacitor according to Embodiment 10 of the present invention;

Fig. 8 is Table 1 showing characteristics of Examples 1 to 11 and Comparison 1 in Embodiment 1 of the present invention;

Fig. 9 is Table 2 showing the measurement results of amounts of residues in Embodiment 2 of the present invention;

Fig. 10 is Table 3 showing the measurement results of static capacitance and ESR level of Examples 12 to 14 and Comparison 2 in Embodiment 9 of the present invention;

Fig. 11 is Table 4 showing the characteristics of Example 16 and Comparisons 3 and 4 in Embodiment 10 of the present invention;

Fig. 12 is a cross sectional view of a conventional solid electrolytic capacitor;

Fig. 13 is a flowchart showing a conventional solid

electrolytic capacitor making method;

Fig. 14 is a front view showing residues deposited on the outer surface of an anode body in the conventional solid electrolytic capacitor making method; and

5 Fig. 15 is a cross sectional view showing residues deposited in the pores of an anode body in the conventional solid electrolytic capacitor making method.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

10 Before the detailed description proceeds, it is noted that like parts are designated by like reference numerals throughout the accompanying drawings.

Preferred embodiments of the solid electrolytic capacitor making method of the present invention will be
15 described in more detail referring to the relevant drawings.

Embodiment 1

Fig. 1 is a flowchart showing a method of producing a solid electrolytic capacitor according to Embodiment 1 of the present invention. The method starts with a forming
20 and sintering step S1 where a metal powder of tantalum with an anode lead line of tantalum inserted therein is pressed into a desired shape which is then sintered to form a porous anode element. A chemical processing step S2 follows where the anode element is subjected to oxidization

with phosphoric acid to form a dielectric oxide coating layer on the outer surface thereof.

5 This is followed by an electrically conductive polymer layer forming step S3 of immersing (in step S31) the anode element with the dielectric oxide coating layer provided thereon into a water solution which contains an electrically conductive polymer having hydrophilic groups in its polymeric structure, and after drawing up the anode element, evaporating the water which serves as a solvent.
10 Then, a heating step S32 follows for forming the electrically conductive polymer layer.

A first solid electrolyte layer forming step S4 follows where the anode element with the electrically conductive polymer layer provided thereon is subjected at
15 its outer surface and in the pores thereof to uniform dispersion of a monomer solution containing a heterocyclic compound or its derivative, and then exposed directly to an oxidizer solution or subjected to uniform dispersion of the oxidizer solution and then exposed to the monomer solution
20 to thereby form a heterocyclic compound layer through the chemical oxidation polymerization (S41). Subsequently, residues deposited on the polymer film during the polymerizing process are removed by rinsing (S42), and then the resultant polymer film is dried out (S43). Thus, the

anode element is coated with the first solid electrolyte layer of the heterocyclic compound.

Next, in a cathode layer forming step S5, the anode element is covered with a cathode layer fabricated by
5 applying and drying a carbon coating and a silver paint coating to thereby fabricate a capacitor element.

An assembling step S6 follows where the anode lead line of the capacitor element is joined by welding to a COM or anode terminal and the cathode layer is joined through
10 an electrically conductive adhesive to a cathode terminal. Then, in a molding step S7, the capacitor element is encapsulated with a resin enclosure by molding an epoxy resin material with the anode terminal and the cathode terminal partially exposed to the outside. At a final step
15 S8, an array of the capacitor elements are separated into chips which are then tested.

This method is high in the production efficiency and can consistently fabricate solid electrolytic capacitors which are enhanced in low impedance characteristic and
20 improved in current leakage with a high static capacitance.

Some examples of the present invention will now be described below.

(Example 1)

A porous anode element was fabricated by press forming

a metal powder of tantalum into a desired shape with an anode lead line of tantalum inserted therein and sintering the resultant shape in the forming and sintering step S1.

Then, in step S2, a dielectric oxide cladding layer
5 was formed on the outer surface of the anode element by an anode oxidation process using a phosphoric acid solution.

For forming an electrically conductive polymer layer in step S3, the anode element with the dielectric oxide cladding layer was immersed (S31) in a water solution which
10 had a surface tension of 70×10^{-3} N/m and contained 10 wt% of poly-aniline derived from a monomer where R in Formula 1 was replaced by an ethyl group, and then the anode element was drawn up to evaporate the water which serves as a solvent. Then, the anode element was heated at 160 °C for
15 5 minutes (S32) to form an electrically conductive polymer layer thereon.

For forming the first solid electrolyte layer in step S4, the anode element had a pyrrole monomer solution dispersed evenly on the outer surface and in the pores
20 thereof and was then exposed directly to an oxidizing solution to form a poly-pyrrole polymer film through a chemical polymerizing process (S41). Thereafter, the dielectric oxide cladding layer on the anode element was repaired with a using an acetic acid solution.

Subsequently, residues generated on the polymer film during the polymerizing process were removed by rinsing (S42) and then the polymer film was dried (S43). This action was repeated three times so that the anode element was finally
5 coated with the first solid electrolyte layer of polypyrrole.

The pyrrole monomer solution was prepared by dissolving 1.0 mol/l of pyrrole and 0.25 mol/l of sodium alkyl-naphthalene-sulfonate as a dopant into a water
10 solution containing 10 wt% of ethylene glycol. The oxidizing solution was prepared by dissolving 0.75 mol/l of iron sulfate (III) as an oxidizer, 0.05 mol/l of sodium alkyl-naphthalene-sulfonate as a dopant, and 0.75 mol/l of sulfuric acid as an additive into a water solution
15 containing 10 wt% of ethylene glycol.

Next, in step S5, the anode element was covered with a carbon coating and a silver paint coating applied and was dried to form a cathode layer. As a result, a capacitor element was fabricated.

20 In the next assembling step S6, the anode lead line of the capacitor element was joined by welding to the COM or anode terminal and the cathode layer was joined through an electrically conductive adhesive to the cathode terminal. This was followed by a molding step S7 where the capacitor

element was encapsulated with a resin enclosure of an epoxy resin material with the anode terminal and the cathode terminal exposed partially to the outside. Finally, in step S8, an array of the elements were separated into chips and tested to form a number of solid electrolytic capacitors.

(Example 2)

A solid electrolytic capacitor was fabricated by the same manner as of Example 1, except that the electrically conductive polymer layer was formed (S3) from a water solution containing 5 wt% of poly-aniline derived from a monomer where R in Formula 1 was replaced by an ethoxy group and that the heating was carried out at 180 °C for 5 minutes.

(Example 3)

A solid electrolytic capacitor was fabricated by the same manner as of Example 1, except that the electrically conductive polymer layer was formed (S3) from a water solution containing 5 wt% of poly-aniline derived from a monomer where R in Formula 1 was replaced by an ethoxy group. Also, in this example 3, the heating (S32) was carried out at 200 °C for 5 minutes.

(Example 4)

A solid electrolytic capacitor was fabricated by the

same manner as of Example 1, except that the electrically
conductive polymer layer was formed from a water solution
containing 5 wt% of poly-aniline derived from a monomer
where R in Formula 1 was hydrogen and that the heating was
5 carried out at 250 °C for 5 minutes.

(Example 5)

A solid electrolytic capacitor was fabricated by the
same manner as of Example 1, except that the electrically
conductive polymer layer was formed from a water solution
10 containing 5 wt% of poly-aniline derived from a monomer
where R in Formula 1 was replaced by a nitro group and that
the heating was carried out at 200 °C for 5 minutes.

(Example 6)

A solid electrolytic capacitor was fabricated by the
15 same manner as of Example 1, except that the electrically
conductive polymer layer was formed from a water solution
containing 5 wt% of poly-aniline derived from a monomer
where R in Formula 1 was replaced by a hydroxyl group and
that the heating was carried out at 200 °C for 5 minutes.

20 (Example 7)

A solid electrolytic capacitor was fabricated by the
same manner as of Example 1, except that the electrically
conductive polymer layer was formed from a water solution
containing 5 wt% of poly-aniline derived from a monomer

where R in Formula 1 was replaced by an ethyl group and that the heating was carried out at 200 °C for 5 minutes.

(Example 8)

5 A solid electrolytic capacitor was fabricated by the same manner as of Example 1, except that the electrically conductive polymer layer was formed from a water solution having a surface tension of 50×10^{-3} N/m added with ethanol.

(Example 9)

10 A solid electrolytic capacitor was fabricated by the same manner as of Example 1, except that the electrically conductive polymer layer was formed from a water solution having a surface tension of 40×10^{-3} N/m added with a fluorine system surfactant (surface active agent).

15 (Example 10)

A solid electrolytic capacitor was fabricated by the same manner as of Example 1, except that the electrically conductive polymer layer was formed from a water solution containing 1 wt% of poly-aniline derived from a monomer
20 where R in Formula 1 was replaced by a methoxy group and that the heating was carried out at 180 °C for 5 minutes.

(Example 11)

A solid electrolytic capacitor was fabricated by the same manner as of Example 1, except that the electrically

conductive polymer layer was formed from a water solution containing 0.5 wt% of poly-aniline derived from a monomer where R in Formula 1 was replaced by a methoxy group and that the heating was carried out at 180 °C for different heating times of 1, 5, 10, 20 and 30 minutes.

(Comparison 1)

A solid electrolytic capacitor was fabricated by the same manner as of Example 1, except that the electrically conductive polymer layer was formed by immersing into a manganese nitrate 30 % water solution, natural drying, and heating at 300 °C for 10 minutes for decomposition to form a manganese dioxide layer.

The solid electrolytic capacitors of Examples 1 to 11 and Comparison 1 were subjected to aging and their characteristics were measured. Resultant measurements are shown in Table 1 in Fig. 8, each measurement being an average of the measurements from ten solid electrolytic capacitors of each type.

The leak current shown in Table 1 is a current level measured one minute after the application of a rated voltage. The withstand voltage is measured at a point of polarization shift during the sweeping at 0.2 V/sec.

As apparent from the measurements of Examples 1 to 11 and Comparison 1 shown in Table 1, the electrically

conductive polymer layer formed by immersing into an electrically conductive polymer water solution having a hydrophilic group in its polymer structure and heating at a temperature of 160 to 250 °C can be minimized in the dissolution into water. Also, as its solid electrolytic layer is formed from a polymerizing solution containing water, the solid electrolytic capacitor can be enhanced in the static capacitance and impedance characteristic.

As Example 8 allows the water solution for the conductive polymer having a hydrophilic group in the polymer structure has a surface tension of 50×10^{-3} N/m, its dielectric oxide cladding layer is higher in the permeability than that of Example 1. Accordingly, the capacitor characteristics can be improved.

Embodiment 2

In the method of Embodiment 1, the rinsing process in step S4 is implemented by a rinsing apparatus shown in Fig. 2 during the formation of the first solid electrolyte layer.

Fig. 2 is a front cross sectional view of the rinsing apparatus for implementing the rinsing step. Shown are capacitor elements 1 (each provided with the first solid electrolyte layer of poly-pyrrole), anode lead lines 2 extending from their respective capacitor elements 1, and a support bar 3 having the anode lead lines 2 of the

capacitor elements 1 joined thereto at equal intervals of a distance by welding.

A shower nozzle 4A is provided above the row of the capacitor elements 1 for rinsing the capacitor elements 1 with a shower of water. More specifically, the shower nozzle 4A has slits or apertures provided therein for applying a shower of water over the capacitor elements 1 aligned below. Also shown are a curtain of water 5 emitted from the shower nozzle 4A, a reservoir 6, an amount of water 7 filled in the reservoir 6, a pump 8 for pumping the water 7 from the reservoir 6 via a conduit 9 to the shower nozzle 4A, a shower chamber 10, and a cover 11.

Using the rinsing apparatus, a shower of water 5 at a pressure of 1.0 kg/cm^2 was emitted from the shower nozzle 4A against the capacitor elements 1 for 10 seconds and paused. Then, this shower rinsing action is repeated again. Also, this action was conducted with different pressures, 0.3, 0.5, 1.0, and 1.5 kg/cm^2 , and their results are shown in the form of amounts of residues in Table 2 in Fig. 9.

It is apparent from Table 2 that the pressure for providing a shower of water from the shower nozzle 4A to the capacitor elements 1 should be not smaller than 0.5 kg/cm^2 .

Fig. 3 illustrates the capacitor elements 1, each with

the first solid electrolyte layer provided thereon after the shower rinsing step. Each of the capacitor elements 1 joined to the support bar 3 has the first solid electrolyte layer of poly-pyrrole formed uniformly thereon and its
5 residues removed off thoroughly.

Since the solid electrolytic capacitor manufacturing method of the present invention includes the rinsing step (S42) for removing any unwanted residues generated during the polymer layer forming step (S41), its resultant solid
10 electrolytic capacitor can be improved in quality with its solid electrolyte layer formed uniformly.

Embodiment 3

As a feature of Embodiment 3 of the present invention, the solid electrolytic capacitor manufacturing method is
15 modified in which the rinsing (S42) for removing unwanted residues includes two steps for removing residues from the outer surface of the anode element and then from the pores of the anode element.

The step of removing residues from the outer surface
20 of the anode element is selected from a shower rinsing process using a shower of liquid such as water, hot water, or organic solvent or air or gas, or an ultrasonic rinsing process using the liquid, or a blasting process.

The step of removing residues from the pores of the

anode element is implemented by either a rinsing process using a shower of liquid such as water, hot water, or organic solvent or an ultrasonic rinsing process. In addition to the feature of Embodiment 2, the feature of this embodiment can ensure fabrication of a solid electrolytic capacitor having a higher degree of performance.

The solid electrolytic capacitor manufacturing method of Embodiment 3 of the present invention will now be described referring to the relevant drawings.

Residues deposited on the polymer layer of poly pyrrole during the first solid electrolyte layer forming step S4 are classified into those on the outer surface of the anode element and those in the pores of the anode element. The residues deposited on the outer surface of the anode element can simply be removed by shower rinsing with water (preferably hot water) or air.

Alternatively, the residues deposited in the pores of the anode element can preferably be removed by an ultrasonic rinsing process. Fig. 3 illustrates an array of the anode elements with residues removed off from their outer surface. Fig. 4 illustrates the anode element with residues removed off from its pores.

Embodiment 4

As a feature of Embodiment 4 of the present invention, the solid electrolytic capacitor manufacturing method is modified in which the first solid electrolyte layer forming step S4 is followed by a second solid electrolyte layer forming step S4' for forming another solid electrolyte layer under different conditions. In addition to the feature of Embodiment 1, the feature of this embodiment can ensure fabrication of a solid electrolytic capacitor having a higher degree of performance.

10 The solid electrolytic capacitor making method of Embodiment 4 of the present invention will now be described referring to the relevant drawings.

Fig. 5 is a flowchart showing the solid electrolytic capacitor manufacturing method of Embodiment 4 of the present invention. The method of Embodiment 4 is a modification of Embodiment 1 where the first solid electrolyte layer forming step S4 is followed by a second solid electrolyte layer forming step S4'. In the second solid electrolyte layer forming step S4', another solid electrolyte layer is formed under specific conditions which are different from those in the first solid electrolyte layer forming step S4.

20 More particularly, the monomer solution used in the second solid electrolyte layer forming step S4' is prepared

by dissolving 0.75 mol/l of pyrrole as a monomer and 0.25 mol/l of sodium alkyl-naphthalene-sulfonate as a dopant into a water solution containing 10 wt% of ethylene glycol. The oxidizing solution is prepared by dissolving 0.75 mol/l of iron sulfate (III) as an oxidizer, 0.05 mol/l of sodium alkyl-naphthalene-sulfonate as a dopant, and 0.75 mol/l of sulfuric acid as an additive into a water solution containing 10 wt% of ethylene glycol.

The solid electrolyte layer formed by the first solid electrolyte layer forming step S4 has the monomer solution dispersed evenly thereon and is then exposed directly to the oxidizing solution to form a polymer layer of poly-pyrrole through a chemical oxidation polymerization process. Then, an abundance of the oxidizing solution is removed by rinsing with water or hot water. Subsequently, the dielectric oxide cladding layer has been restored, and then rinsed with water or hot water, and dried out. Thus, the anode element is covered with the solid electrolyte layer of poly-pyrrole.

The second solid electrolyte layer forming step S4' is differentiated from the first solid electrolyte layer forming step S4 by the fact that the concentration of the pyrrole monomer solution is modified. Alternatively, the concentration of the pyrrole monomer solution may be

declined in the second solid electrolyte layer forming step.

As the second solid electrolyte layer forming step S4',
unlike the first solid electrolyte layer forming step S4,
downwardly controls the chemical oxidation polymerization
5 action, its resultant solid electrolyte layer of
electrically conductive polymer can be uniform throughout
the pores in the anode element. Hence, this contributes to
the production of a solid electrolytic capacitor having a
higher degree of performance.

10 Embodiment 5

As a feature of Embodiment 5 of the present invention,
the second solid electrolyte layer forming step S4' is
implemented by repeating at least two or more times a
procedure of the anode element being immersed into the
15 monomer solution for a predetermined time period, then
immersed into the oxidizing solution for a predetermined
time period, and drawn up and held in the air for a
predetermined time period. Thus, in addition to the
feature of Embodiment 4, the feature of this embodiment can
20 ensure fabrication of a solid electrolytic capacitor having
a higher degree of performance.

The solid electrolytic capacitor making method of
Embodiment 5 of the present invention will now be described
referring to the relevant drawings.

The second solid electrolyte layer forming step S4' of Embodiment 4 is implemented by dispersing the monomer solution uniformly and exposing directly to the oxidizing solution to form a polymer layer of poly-pyrrole through a chemical oxidation polymerization process. At this time, after the anode element has been immersed into the monomer solution and then into the oxidizing solution, it is dried and held in the air for a predetermined time length.

This allows the chemical oxidation polymerization process to be fully conducted in the pores of the anode element. Also, the chemical oxidation polymerization process can be accelerated when temperature of the air where the anode element is held is made higher than that of the oxidizing solution.

Then, an abundance of the oxidizing solution is removed by rinsing with water or hot water. After its dielectric oxide cladding layer is restored, the anode element is rinsed with water or hot water and dried. After repeating the above procedure, the anode element can be covered uniformly with the solid electrolyte layer.

Embodiment 6

As a feature of Embodiment 6 of the present invention, the solid electrolytic capacitor manufacturing method is modified where the first solid electrolyte layer forming

step S4 is followed by a second solid electrolyte forming step S4' for forming another solid electrolyte layer under different conditions and a third solid electrolyte layer forming step S4'' for forming a further solid electrolyte layer of a different electrically conductive polymer. In addition to the feature of Embodiment 4, the feature of this embodiment can ensure fabrication of a solid electrolytic capacitor having a higher degree of performance.

10 The solid electrolytic capacitor manufacturing method of Embodiment 6 of the present invention will now be described referring to the relevant drawings.

15 Fig. 6 is a flowchart showing the solid electrolytic capacitor manufacturing method of Embodiment 6 of the present invention. The method of Embodiment 6 has the second solid electrolyte layer forming step S4' and the third solid electrolyte layer forming step S4'' provided after the first solid electrolyte layer forming step S4 of Embodiment 1. The third solid electrolyte layer forming step S4'' is provided for forming a solid electrolyte layer of an electrically conductive polymer which is different from that of the first solid electrolyte layer forming step S4.

20 More particularly, the first solid electrolyte layer

forming step S4 is implemented by the anode element with the dielectric oxide cladding layer provided thereon having the pyrrole monomer solution dispersed evenly on the surface thereof and being exposed directly to the oxidizing solution or having the oxidizing solution dispersed evenly thereon and being exposed directly to the pyrrole monomer solution to thereby form a polymer layer of poly-pyrrole through a chemical oxidation polymerization process as described for Embodiment 1.

Then, an abundance of the oxidizing solution is removed by rinsing with water or hot water and then the dielectric oxide cladding layer is restored. Subsequently, the residues deposited on the polymer layer during the polymerization process are removed by rinsing. After the polymer layer has been dried out, the anode element is covered with the solid electrolyte layer of poly-pyrrole.

This is followed by the second solid electrolyte layer forming step S4'. In the same manner as described in Embodiment 4, the solid electrolyte layer formed by the first solid electrolyte layer forming step S4 has the pyrrole monomer solution dispersed evenly on the surface thereof and being exposed directly to the oxidizing solution or having the oxidizing solution dispersed thereon and being exposed directly to the pyrrole monomer solution

to form a polymer layer of poly-pyrrole through a chemical oxidation polymerization process.

Then, an abundance of the oxidizing solution is removed by rinsing with water or hot water. Then, the dielectric oxide cladding layer is restored, rinsed with water or hot water, and dried out. Thus, the anode element is covered with the solid electrolyte layer of poly-pyrrole.

Then in the third solid electrolyte layer forming step S4'', a suspension is prepared by dissolving 1.0 mol/l of ethylene dioxythiophene, 0.75 mol/l of P-toluene ferrous sulfonate as an oxidizer, and 0.15 mol/l of sodium alkyl-naphthalene-sulfonate as a dopant into a water solution containing 10 wt% of ethylene glycol.

The anode element with the solid electrolyte layer formed by the second solid electrolyte layer forming step S4' is then immersed into the suspension for a predetermine time length, then drawn up, and held for a predetermined time length. Thereafter, an abundance of the suspension is removed by rinsing with water or hot water.

After the dielectric oxide cladding layer has been restored, rinsed with water or hot water, and dried, the anode element is covered with a solid electrolyte layer of poly-thiophene.

Since the third solid electrolyte layer is formed of

poly-thiophene selectively using as an electrically conductive polymer, a resultant solid electrolytic capacitor of Embodiment 6 can be improved in performance.

Embodiment 7

5 As a feature of Embodiment 7 different from that of Embodiment 6 of the present invention, the third solid electrolyte layer forming step S4'' is implemented by electrolytic polymerization to improve the polymerization speed. Also, even in the case where a capacitor is left in
10 an initial and high temperature conditions, a solid electrolytic capacitor can be improved in low impedance characteristic.

 The solid electrolytic capacitor manufacturing method of Embodiment 7 of the present invention will now be
15 described.

 The solid electrolytic capacitor of Embodiment 7 is fabricated in the same manner as that of Embodiment 6 except for the following procedure. That is, in this Embodiment 7, in the third solid electrolyte layer forming
20 step S4'', a suspension is prepared by dissolving 0.5 mol/l of ethylene dioxythiophene, and 0.1 mol/l of chloride alkyl-naphthalene-sulfonate as a dopant into a water solution containing isopropyl alcohol for stabilization thereof.

Then the anode element with the solid electrolyte layer is immersed into the water solution where a working electrode is contacted to a part of the electrically conductive polymer layer so that the electrolytic polymerization is conducted under application of a constant voltage of 3V for 30 minutes. Thus, the electrically conductive polymer layer of polyethylene dioxythiophene is evenly deposited.

By this arrangement, a resultant solid electrolytic capacitor of Embodiment 7 can be improved in performance in addition to an effective action of Embodiment 6.

Embodiment 8

As a feature of Embodiment 8 of the present invention, the third solid electrolyte layer forming step S4'' is implemented by repeating at least two or more times a procedure of the anode element being immersed into the suspension containing the monomer, oxidizer, and electrically conductive polymer for a predetermined time length, and then drawn up and held in the air for a predetermined time length.

Thus, in addition to the feature of Embodiment 6, the feature of this embodiment can ensure fabrication of a solid electrolytic capacitor having a higher degree of performance.

The solid electrolytic capacitor manufacturing method of Embodiment 8 of the present invention will now be described.

5 The third solid electrolyte layer forming step S4'' as described in Embodiment 6 is implemented by the procedure such that the anode element is immersed into the suspension for a predetermined time length, drawn up, held for a specific time length, rinsed with water or hot water to remove an abundance of the suspension, and then rinsed
10 again with water or hot water, and dried out. This procedure is repeated several times to form the solid electrolyte layer of poly-thiophene more uniformly.

Embodiment 9

As a specific feature of Embodiment 9 of the present
15 invention, the solid electrolytic capacitor manufacturing method of any of Embodiments 1, 4, and 6 is modified as following. That is, after the cathode layer forming step S5 is carried out, a step of heating the anode element with the solid electrolyte layer provided thereon is carried out.

20 This allows unwanted organic residues deposited on the polymer layer to be completely removed off while the solid electrolyte layer remains solid, hence contributing to the production of a solid electrolytic capacitor improved in capacitance and ESR level.

The solid electrolytic capacitor manufacturing method of Embodiment 9 of the present invention will now be described in more detail in the form of examples.

(Example 12)

5 The same method as of Embodiment 1 was used for fabricating a solid electrolytic capacitor except for the following procedure. That is, after a cathode layer is formed in step S5 subsequent to forming a first solid electrolyte layer in step S4, the anode element having the
10 first solid electrolyte layer formed thereon was subjected to a heating process at 250 °C.

(Example 13)

 The same method as of Embodiment 4 was used for fabricating a solid electrolytic capacitor except for the
15 following procedure. That is, after a cathode layer is formed in step S5 subsequent to forming a second solid electrolyte layer in step S4', the anode element having the second solid electrolyte layer formed thereon was subjected to a heating process at 250 °C.

20 (Example 14)

 The same method as of Embodiment 6 was used for fabricating a solid electrolytic capacitor except for the following procedure. . That is, after a cathode layer is formed in step S5 subsequent to forming a third solid

electrolyte layer in step S4'', the anode element having the third solid electrolyte layer formed thereon was subjected to a heating process at 250 °C.

(Comparison 2)

5 A solid electrolytic capacitor was fabricated using the above mentioned conventional method.

As the solid electrolytic capacitors of Examples 12 to 14 and Comparison 2 were measured in the static capacitance at 120 Hz and the ESR level at 100 kHz, their measurements
10 are shown in Table 3 in Fig. 10.

As apparent from Table 3, the solid electrolytic capacitors of Examples 12 to 14 are higher in capacitance and ESR level than those of Comparison 2.

Since the anode element with the solid electrolyte
15 layer provided thereon is heated after the cathode layer forming step, its solid electrolyte layer can remain solid and high in the bonding strength, thus contributing to the production of a solid electrolytic capacitor increased in capacitance and ESR level.

20 The heating may preferably be conducted at a temperature ranging from 230 to 280 °C. If the temperature for the heating is not higher than 230 °C, the solid electrolyte layer will hardly remain solid. When the temperature exceeds 280 °C, the solid electrolyte layer

will be deteriorated thus declining the capacitance and the ESR level.

Embodiment 10

5 A specific feature of Embodiment 10 of the present invention resides in the fact that the residues deposited on the first solid electrolyte layer are not greater than 5 % by weight. With a minimum of the residues, the solid electrolytic capacitor can be improved in volumetric compactness.

10 The solid electrolytic capacitor of Embodiment 10 will now be described in more detail.

According to Embodiment 10 of the present invention, the residues deposited on the polymer layer during the first solid electrolyte layer forming step S4 are minimized
15 and their resultant measurements are shown by impedance values in relation to frequencies (Hz) in Fig. 7.

As apparent from Fig. 7, the declination in the ESR level can be minimum when the residues deposited on the polymer layer during the first solid electrolyte layer
20 forming step are not greater than 5 % by weight.

Embodiment 11

A specific feature of Embodiment 11 resides in the fact that the first solid electrolyte layer forming step S4 is implemented by electrolytic polymerization to improve

the polymerization speed. Also, in an initial stage and even in the case where a capacitor is left in a high temperature condition, a solid electrolytic capacitor can be improved in low impedance characteristic.

5 The solid electrolytic capacitor manufacturing method of Embodiment 11 of the present invention will now be described.

(Example 15)

10 An aluminum etched foil provided with a lead is used as an anode element. The anode element is subjected to an oxidation process using a water solution containing 3% adipic acid ammonium to thereby form a dielectric oxide cladding layer on the outer surface of the anode element.

15 Next, for forming an electrically conductive polymer layer in step S3, the anode element with the dielectric oxide cladding layer was immersed (S31) in a water solution which had a surface tension of 70×10^{-3} N/m and contained 5 wt% of poly-aniline derived from a monomer where R in Formula 1 was replaced by an ethoxy group, and then the
20 anode element was drawn up to evaporate the water which serves as a solvent. Then, the anode element was heated at 200 °C for 5 minutes (S32) to thereby form an electrically conductive polymer layer thereon.

For forming the first solid electrolyte layer in step

S4, 0.5 mol/l of pyrrole monomer and 0.1 mol/l of sodium alkyl-naphthalene-sulfonate are previously mixed, and then water serving as a solvent and propyl phosphoric ester serving as a pH adjustment are added thereto to prepare a
5 polymerization solution of pH 2. By using the polymerization solution, an electrode for starting polymerization is set close to the aluminum etched foil and the electrolytic polymerization is conducted with an electrolytic voltage of 2V. Subsequently, residues
10 generated on the polymer film during the polymerizing process are removed by rinsing (S42) and then the polymer film is dried (S43).

Next, in order to form a cathode layer in step S5, the anode element is covered with a carbon coating and a silver
15 paint coating applied and is dried. As a result, a capacitor element is fabricated. Thereafter, the capacitor element is encapsulated with a resin enclosure of an epoxy resin material.

(Comparison 3)

20 In Comparison 3, in order for forming the first solid electrolyte layer in step S4, the anode element had a pyrrole monomer solution dispersed evenly on the outer surface and in the pores thereof and was then exposed directly to an oxidizing solution to form a poly-pyrrole

polymer film through a chemical polymerizing process (S41).

Thereafter, the dielectric oxide cladding layer on the anode element was repaired using an acetic acid solution. Subsequently, residues generated on the polymer film during the polymerizing process were removed by rinsing (S42) and then the polymer film was dried (S43). This action was repeated three times so that the anode element was finally coated with the first solid electrolyte layer of polypyrrole. The other processes are the same as those of Example 15.

The pyrrole monomer solution was prepared by dissolving 1.0 mol/l of pyrrole and 0.25 mol/l of sodium alkyl-naphthalene-sulfonate as a dopant into a water solution containing 10 wt% of ethylene glycol. The oxidizing solution was prepared by dissolving 0.75 mol/l of iron sulfate (III) as an oxidizer, 0.05 mol/l of sodium alkyl-naphthalene-sulfonate as a dopant, and 0.75 mol/l of sulfuric acid as an additive into a water solution containing 10 wt% of ethylene glycol.

(Comparison 4)

A solid electrolytic capacitor was fabricated by the same manner as of Example 15 except the following step. That is, in Comparison 4, the electrically conductive polymer layer was formed by immersing into a manganese

nitrate 30 % water solution, natural drying, and heating at 300 °C for 10 minutes for decomposition to form a manganese dioxide layer.

5 The solid electrolytic capacitors of Example 15 and Comparisons 3 and 4 were subjected to aging and their characteristics were measured. Resultant measurements are shown in Table 4 in Fig. 11, each measurement being an average of the measurements from ten solid electrolytic capacitors of each type.

10 As apparent from Table 4, as the solid electrolytic capacitors of Example 15 were fabricated through electrolytic polymerization using a polymerization solution of a low pH value, the impedance and leakage characteristics are remarkably improved compared to the
15 solid electrolytic capacitors of Comparison 3 which were fabricated through chemical oxidation polymerization.

 Also, the static capacitance and leakage current characteristics are remarkably improved in Example 15 compared to the solid electrolytic capacitors of Comparison
20 4 which were fabricated by forming a solid electrolyte layer on the surface of a manganese dioxide layer through electrolytic polymerization.

 As set forth above, the present invention provides the steps of: immersing the anode element into a water solution

of electrically conductive polymer containing a hydrophilic group in the polymer structure and then drawing up and heating the same to form an electrically conductive polymer layer on the dielectric oxide cladding layer; and coating
5 the electrically conductive polymer layer with a solution containing a monomer of a heterocyclic compound or its derivative, polymerizing the monomer in the solution to form a polymer layer, rinsing the anode element to remove residues deposited on the polymer layer, and drying the
10 anode element to form a first solid electrolyte layer, whereby residues deposited on the solid electrolyte layer during the polymerization process can be removed by an appropriate means such as rinsing with a shower during the solid electrolyte layer forming step.

15 Accordingly, as its solid electrolyte layer is formed uniform, the solid electrolytic capacitor can be improved in reliability.

 In addition, the step of providing the first electrolyte layer is followed by a step of providing a
20 second solid electrolyte layer under different conditions. Alternatively, the step of providing the first electrolyte layer is followed by a step of providing a second solid electrolyte layer under different conditions and then a step of providing a third electrolyte layer of a different

electrically conductive polymer.

Those features can improve the capacitance characteristic and the ESR level, thus contributing to production of a solid electrolytic capacitor having a
5 higher degree of reliability.

Moreover, as the anode body covered with the solid electrolyte layer is heated after the cathode layer forming step, its solid electrolyte layer remains solid and residues on its polymer layer can completely be removed.
10 Accordingly, the solid electrolytic capacitor can be enhanced in capacitance characteristic and in ESR level.

Although the present invention has been described in connection with the preferred embodiments thereof with reference to the accompanying drawings, it is to be noted
15 that various changes and modifications will be apparent to those skilled in the art. Such changes and modifications are to be understood as included within the scope of the present invention as defined by the appended claims, unless they depart therefrom.



WHAT IS CLAIMED IS:

1. A method of manufacturing a solid electrolytic capacitor comprising the steps of:

5 providing a dielectric oxide film on a surface of an anode element made of a valve metal;

immersing the anode element into a water solution of electrically conductive polymer containing a hydrophilic group in a polymer structure and then drawing up the anode element and heating the same to form an electrically
10 conductive polymer layer on the dielectric oxide cladding layer;

coating the electrically conductive polymer layer with a solution containing a monomer of a heterocyclic compound or its derivative, and polymerizing the monomer in the
15 solution to form a polymer layer, rinsing the anode element to remove residues deposited on the polymer layer, and drying the anode element to form a first solid electrolyte layer; and

20 providing a cathode layer on the first solid electrolyte layer.

2. A method of manufacturing a solid electrolytic capacitor according to claim 1, wherein the electrically conductive polymer having a hydrophilic group in the

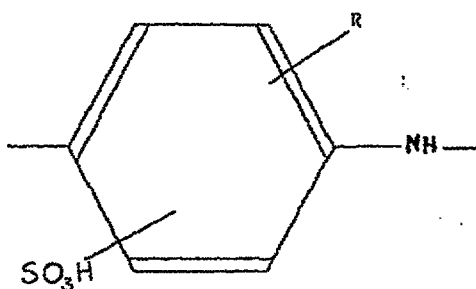


polymer structure is a derivative of aniline, pyrrole, thiophene, or furan of the monomer.

3. A method of manufacturing a solid electrolytic capacitor according to claim 2, wherein the electrically conductive polymer having a hydrophilic group in the polymer structure is a self-doping type electrically conductive polymer having a sulfonic group.

4. A method of manufacturing a solid electrolytic capacitor according to claim 3, wherein the electrically conductive polymer having a hydrophilic group in the polymer structure is an aniline derivative expressed by Formula 2.

(Formula 2)



5 A method of manufacturing a solid electrolytic capacitor according to claim 1, wherein the water solution of the electrically conductive polymer having a hydrophilic



group in the polymer structure has a surface tension of not higher than 70×10^{-3} N/m.

6. A method of manufacturing a solid electrolytic capacitor according to claim 1, wherein the heating is conducted at a temperature ranging from 160 to 250 °C.

7. A method of manufacturing a solid electrolytic capacitor according to claim 1, wherein the formation of the first solid electrolyte layer is implemented by a chemical oxidation polymerization process using an oxidizer.

8. A method of manufacturing a solid electrolytic capacitor according to claim 7, wherein the step of providing the first solid electrolyte layer is implemented by repeating at least two or more times a procedure of: immersing the anode element into one of a monomer solution and an oxidizing solution for a predetermined time and then into the other solution for a predetermined time to form a polymer layer and subsequently restoring the dielectric oxide cladding layer.

9. A method of manufacturing a solid electrolytic capacitor according to claim 8, wherein the temperature of



the oxidizing solution is lower than that when held in the air.

10. A method of manufacturing a solid electrolytic
5 capacitor according to claim 1, wherein the step of providing the first solid electrolyte layer is implemented by electrolytic polymerization.

11. A method of manufacturing a solid electrolytic
10 capacitor according to claim 10, wherein the electrolytic polymerization is performed using a water solution of pH not greater than pH 5 which contains at least a monomer of a heterocyclic compound or its derivative, a pH adjustment agent and water.

15

12. A method of manufacturing a solid electrolytic
capacitor according to claim 1, wherein the rinsing for removing residues is implemented by removing the residues at least either from the outer surface of the anode element
20 or from the pores in the anode element.

13. A method of manufacturing a solid electrolytic
capacitor according to claim 12, wherein the rinsing for removing residues either from the outer surface of the



anode element or the pores in the anode element is implemented by rinsing with a shower of liquid including water, hot water, or organic solvent or air or gas, by ultrasonic rinsing, or by blasting.

5

14. A method of manufacturing a solid electrolytic capacitor according to claim 1, wherein the step of providing the first solid electrolyte layer is followed by a step of providing a second solid electrolyte layer under a different condition from that of providing the first solid electrolyte layer.

15. A method of manufacturing a solid electrolytic capacitor according to claim 1, wherein the step of providing the first solid electrolyte layer is followed by a step of providing a second solid electrolyte layer under a different condition from that of providing the first solid electrolyte layer and then followed by a step of providing a third solid electrolyte layer of an electrically conductive polymer different from the first and second solid electrolyte layers.

16. A method of manufacturing a solid electrolytic capacitor according to claim 15, wherein the step of



providing the third solid electrolyte layer is implemented by repeating at least one or more times a procedure of immersing the anode element into a suspension containing a monomer, an oxidizer, and an electrically conductive polymer in particle form for a predetermined time and after
5 drawing up from the suspension, holding the same outside the suspension for a predetermined time.

17. A method of manufacturing a solid electrolytic capacitor according to claim 16, wherein the suspension is
10 prepared by mixing a predetermined amount of monomer and a predetermined amount of oxidizer to form electrically conductive polymer particles and adding the monomer.

15 18. A method of manufacturing a solid electrolytic capacitor according to claim 15, wherein the step of providing the third solid electrolyte layer is implemented by electrolytic polymerization.

20 19. A method of manufacturing a solid electrolytic capacitor according to claim 18, wherein the electrolytic polymerization is performed using a water solution of pH not greater than pH 5 which contains at least a monomer of a heterocyclic compound or its derivative, a pH adjustment



agent and water

20. A method of manufacturing a solid electrolytic capacitor according to any of claims 1, 14 or 15, wherein
5 the step of providing the first solid electrolyte layer includes restoring the dielectric oxide film prior to the rinsing of the polymer film for removing the residues.

21. A method of manufacturing a solid electrolytic
10 capacitor according to any of claims 1, 14 or 15, wherein the step of providing the cathode layer is followed by heating again.

22. A method of manufacturing a solid electrolytic
15 capacitor according to claim 21, wherein the heating is conducted at a temperature ranging from 230 to 280 °C.

23. A solid electrolytic capacitor fabricated by the solid electrolytic capacitor manufacturing method defined
20 in any of claims 1 to 22.

24. A solid electrolytic capacitor according to claim 23, wherein the residues deposited on the electrically conductive polymer layer are smaller than 5 % by weight.