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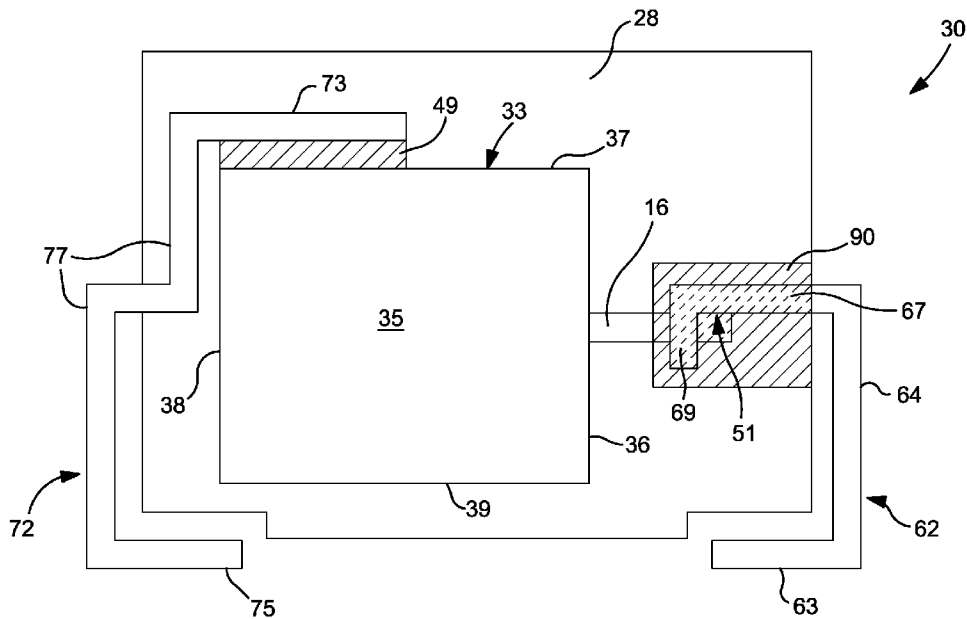


FIG. 1

(57) Abstract: A solid electrolytic capacitor containing a capacitor element is provided. The capacitor element contains a sintered porous anode body, a dielectric that overlies the anode body, and a solid electrolyte that overlies the dielectric. An anode lead extends from the front surface of the capacitor element in the longitudinal direction. An anode termination is in contact with the anode lead at a connection region, wherein the ratio of the distance between the connection region and the front surface of the capacitor element to the length of the capacitor is 0.13 or more. A cathode termination is in electrical connection with the solid electrolyte and a casing material encapsulates the capacitor element and anode lead. Further, an interfacial coating that is disposed on at least a portion of the anode termination and/or cathode termination and is in contact with the casing material.



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SOLID ELECTROLYTIC CAPACITOR

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Cross Reference to Related Application

The present application claims filing benefit of United States Provisional Patent Application Serial No. 62/687,974 having a filing date of June 21, 2018, which is incorporated herein by reference in its entirety.

Background of the Invention

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Electrolytic capacitors (e.g., tantalum capacitors) are increasingly being used in the design of circuits due to their volumetric efficiency, reliability, and process compatibility. For example, one type of capacitor that has been developed is a solid electrolytic capacitor that includes a tantalum anode, dielectric layer, and conductive polymer solid electrolyte. To help protect the capacitor from the exterior environment and provide it with good mechanical stability, the capacitor element is also encapsulated with a casing material (e.g., epoxy resin) so that a portion of the anode and cathode terminations remain exposed for mounting to a surface. Unfortunately, it has been discovered that high temperatures that are often used during manufacture of the capacitor (e.g., reflow) can cause residual moisture to vaporize as steam, which may exit the case with considerable force and cause micro-cracks to form in the casing material. These micro-cracks can lead to delamination of the casing material from the capacitor element and also a rapid deterioration of the electrical properties, particularly when the capacitor is exposed to high temperatures. As such, a need exists for an improved solid electrolytic capacitor that exhibits relatively stable electrical properties at high temperatures.

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Summary of the Invention

In accordance with one embodiment of the present invention, a solid electrolytic capacitor is disclosed that has a length in a longitudinal direction and contains a capacitor element having opposing front and rear surfaces, opposing upper and lower surfaces, and opposing side surfaces. The capacitor element contains a sintered porous anode body, a dielectric that overlies the anode body, and a solid electrolyte that overlies the dielectric. An anode lead extends from the front surface of the capacitor element in the longitudinal direction. An anode

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termination is in contact with the anode lead at a connection region, wherein the ratio of the distance between the connection region and the front surface of the capacitor element to the length of the capacitor is 0.13 or more. A cathode termination is in electrical connection with the solid electrolyte and a casing material encapsulates the capacitor element and anode lead and leaves exposed at least a portion of the anode termination and cathode termination for external contact. Further, an interfacial coating that is disposed on at least a portion of the anode termination and/or cathode termination and is in contact with the casing material.

10 Other features and aspects of the present invention are set forth in greater detail below.

Brief Description of the Drawing

A full and enabling disclosure of the present invention, including the best mode thereof, directed to one of ordinary skill in the art, is set forth more particularly in the remainder of the specification, which makes reference to the appended drawing in which:

Fig. 1 is a cross-sectional view of one embodiment of a solid electrolytic capacitor that may be formed in accordance with the present invention.

20 Repeat use of references characters in the present specification and drawing is intended to represent same or analogous features or elements of the invention.

Detailed Description of Representative Embodiments

It is to be understood by one of ordinary skill in the art that the present discussion is a description of exemplary embodiments only, and is not intended as limiting the broader aspects of the present invention, which broader aspects are embodied in the exemplary construction.

30 Generally speaking, the present invention is directed to a solid electrolytic capacitor that contains a capacitor element having opposing front and rear surfaces, opposing upper and lower surfaces, and opposing side surfaces. The capacitor element includes a porous anode body, dielectric overlying the anode body, and solid electrolyte overlying the dielectric. A cathode termination is in electrical contact with the solid electrolyte. Further, an anode lead is in electrical contact with the anode body and extends from a front surface of the capacitor

element and contacted with an anode termination at a connection region. A casing material encapsulates the capacitor element and anode lead and leaves exposed at least a portion of the anode termination and cathode termination for external contact. An interfacial coating is also disposed on at least a portion of the anode termination and/or cathode termination and is in contact with the casing material.

Through selective control over the particular manner in which the components of the capacitor are arranged and the nature of the materials used to form the capacitor, the present inventors have discovered that a capacitor can be formed that can excellent electrical properties even when exposed to high humidity levels and/or high temperatures. Relative to the length of the capacitor, for example, the distance between the connection region (e.g., where the anode lead contacts the anode termination) and the front surface of the capacitor element may be relatively large. Without intending to be limited by theory, it is believed that this can limit the degree of which ions generated under high humidity levels and/or temperatures are able to come into contact with the solid electrolyte. For example, the ratio of the distance between the connection region and front surface of the capacitor element to the length of the capacitor element is typically about 0.13 or more, in some embodiments about 0.14 or more, in some embodiments about 0.15 or more, and in some embodiments, from about 0.16 to about 0.5. The distance between the connection region to the front surface may vary based on the case size, but typically ranges from about 1 to about 2 millimeters, in some embodiments from about 1 to about 1.8 millimeters, and in some embodiments, from about 1.1 to about 1.6 millimeters. The length of the capacitor likewise typically ranges from about 1 to about 15 millimeters, in some embodiments from about 2 to about 15 millimeters, in some embodiments from about 2 to about 12 millimeters, and in some embodiments, from about 2 to about 8 millimeters.

The resulting electrical properties of the capacitor may be good and remain stable under various conditions. For example, the capacitor may exhibit a relatively low equivalence series resistance ("ESR"), such as about 200 mohms, in some embodiments less than about 150 mohms, in some embodiments from about 0.1 to about 125 mohms, and in some embodiments, from about 1 to about 100 mohms, measured at an operating frequency of 100 kHz and temperature of 23°C. The capacitor may also exhibit a dry capacitance of about 30 nanoFarads per

square centimeter (“nF/cm²”) or more, in some embodiments about 100 nF/cm² or more, in some embodiments from about 200 to about 3,000 nF/cm², and in some embodiments, from about 400 to about 2,000 nF/cm², measured at a frequency of 120 Hz at temperature of 23°C. Notably, such electrical properties (e.g., ESR and/or capacitance) can still remain stable even at high temperatures. For example, the capacitor may exhibit an ESR and/or capacitance value within the ranges noted above even after being exposed to a temperature of from about 80°C or more, in some embodiments from about 100°C to about 150°C, and in some embodiments, from about 105°C to about 130°C (e.g., 105°C or 125°C) for a substantial period of time, such as for about 100 hours or more, in some embodiments from about 150 hours to about 3000 hours, and in some embodiments, from about 200 hours to about 2500 hours (e.g., 240 hours). In one embodiment, for example, the ratio of the ESR and/or capacitance value of the capacitor after being exposed to the high temperature (e.g., 125°C) for 240 hours to the initial ESR and/or capacitance value of the capacitor (e.g., at 23°C) is about 2.0 or less, in some embodiments about 1.5 or less, and in some embodiments, from 1.0 to about 1.3. The capacitor may also exhibit an ESR and/or capacitance value within the ranges noted above after being exposed to a high relative humidity level, either at room temperature or a high temperature (e.g., 85°C or 125°C). Such high relative humidity levels may, for instance, be about 40% or more, in some embodiments about 45% or more, in some embodiments about 50% or more, and in some embodiments, about 70% or more (e.g., about 85% to 100%) for a substantial period of time as noted above. Relative humidity may, for instance, be determined in accordance with ASTM E337-02, Method A (2007). In one embodiment, for example, the ratio of the ESR and/or capacitance value of the capacitor after being exposed to high humidity (e.g., 85%) for 240 hours to the initial ESR and/or capacitance value of the capacitor is about 2.0 or less, in some embodiments about 1.5 or less, and in some embodiments, from 1.0 to about 1.3.

In addition, the capacitor may also exhibit a DCL of only about 50 microamps (“μA”) or less, in some embodiments about 40 μA or less, in some embodiments about 20 μA or less, and in some embodiments, from about 0.1 to about 10 μA. Further, the capacitor may exhibit a high percentage of its wet capacitance, which enables it to have only a small capacitance loss and/or

fluctuation in the presence of atmosphere humidity. This performance characteristic is quantified by the "capacitance recovery", which is determined by the equation:

$$\text{Recovery} = (\text{Dry Capacitance} / \text{Wet Capacitance}) \times 100$$

5 The capacitor may exhibit a capacitance recovery of about 50% or more, in some embodiments about 60% or more, in some embodiments about 70% or more, and in some embodiments, from about 80% to 100%.

Various embodiments of the capacitor will now be described in more detail.

I. Capacitor Element

10 A. Anode Body

The capacitor element includes an anode that contains a dielectric formed on a sintered porous body. The porous anode body may be formed from a powder that contains a valve metal (i.e., metal that is capable of oxidation) or valve metal-based compound, such as tantalum, niobium, aluminum, hafnium, titanium, alloys thereof, oxides thereof, nitrides thereof, and so forth. The powder is typically formed from a reduction process in which a tantalum salt (e.g., potassium fluorotantalate (K_2TaF_7), sodium fluorotantalate (Na_2TaF_7), tantalum pentachloride ($TaCl_5$), etc.) is reacted with a reducing agent. The reducing agent may be provided in the form of a liquid, gas (e.g., hydrogen), or solid, such as a metal (e.g., sodium), metal alloy, or metal salt. In one embodiment, for instance, a tantalum salt (e.g., $TaCl_5$) may be heated at a temperature of from about 900°C to about 2,000°C, in some embodiments from about 1,000°C to about 1,800°C, and in some embodiments, from about 1,100°C to about 1,600°C, to form a vapor that can be reduced in the presence of a gaseous reducing agent (e.g., hydrogen).
25 Additional details of such a reduction reaction may be described in WO 2014/199480 to Maeshima, et al. After the reduction, the product may be cooled, crushed, and washed to form a powder.

The specific charge of the powder typically varies from about 2,000 to about 600,000 microFarads*Volts per gram (" $\mu F \cdot V/g$ ") depending on the desired application. For instance, in certain embodiments, a high charge powder may be employed that has a specific charge of from about 100,000 to about 550,000 $\mu F \cdot V/g$, in some embodiments from about 120,000 to about 500,000 $\mu F \cdot V/g$, and in some embodiments, from about 150,000 to about 400,000 $\mu F \cdot V/g$. In other

embodiments, a low charge powder may be employed that has a specific charge of from about 2,000 to about 100,000 $\mu\text{F}\cdot\text{V}/\text{g}$, in some embodiments from about 5,000 to about 80,000 $\mu\text{F}\cdot\text{V}/\text{g}$, and in some embodiments, from about 10,000 to about 70,000 $\mu\text{F}\cdot\text{V}/\text{g}$. As is known in the art, the specific charge may be
5 determined by multiplying capacitance by the anodizing voltage employed, and then dividing this product by the weight of the anodized electrode body.

The powder may be a free-flowing, finely divided powder that contains primary particles. The primary particles of the powder generally have a median size (D50) of from about 5 to about 500 nanometers, in some embodiments from
10 about 10 to about 400 nanometers, and in some embodiments, from about 20 to about 250 nanometers, such as determined using a laser particle size distribution analyzer made by BECKMAN COULTER Corporation (e.g., LS-230), optionally after subjecting the particles to an ultrasonic wave vibration of 70 seconds. The primary particles typically have a three-dimensional granular shape (e.g., nodular
15 or angular). Such particles typically have a relatively low "aspect ratio", which is the average diameter or width of the particles divided by the average thickness ("D/T"). For example, the aspect ratio of the particles may be about 4 or less, in some embodiments about 3 or less, and in some embodiments, from about 1 to about 2. In addition to primary particles, the powder may also contain other types
20 of particles, such as secondary particles formed by aggregating (or agglomerating) the primary particles. Such secondary particles may have a median size (D50) of from about 1 to about 500 micrometers, and in some embodiments, from about 10 to about 250 micrometers.

Agglomeration of the particles may occur by heating the particles and/or
25 through the use of a binder. For example, agglomeration may occur at a temperature of from about 0°C to about 40°C, in some embodiments from about 5°C to about 35°C, and in some embodiments, from about 15°C to about 30°C. Suitable binders may likewise include, for instance, poly(vinyl butyral); poly(vinyl acetate); poly(vinyl alcohol); poly(vinyl pyrrolidone); cellulosic polymers, such as
30 carboxymethylcellulose, methyl cellulose, ethyl cellulose, hydroxyethyl cellulose, and methylhydroxyethyl cellulose; atactic polypropylene, polyethylene; polyethylene glycol (e.g., Carbowax from Dow Chemical Co.); polystyrene, poly(butadiene/styrene); polyamides, polyimides, and polyacrylamides, high

molecular weight polyethers; copolymers of ethylene oxide and propylene oxide; fluoropolymers, such as polytetrafluoroethylene, polyvinylidene fluoride, and fluoroolefin copolymers; acrylic polymers, such as sodium polyacrylate, poly(lower alkyl acrylates), poly(lower alkyl methacrylates) and copolymers of lower alkyl acrylates and methacrylates; and fatty acids and waxes, such as stearic and other soapy fatty acids, vegetable wax, microwaxes (purified paraffins), etc.

The resulting powder may be compacted to form a pellet using any conventional powder press device. For example, a press mold may be employed that is a single station compaction press containing a die and one or multiple punches. Alternatively, anvil-type compaction press molds may be used that use only a die and single lower punch. Single station compaction press molds are available in several basic types, such as cam, toggle/knuckle and eccentric/crank presses with varying capabilities, such as single action, double action, floating die, movable platen, opposed ram, screw, impact, hot pressing, coining or sizing. The powder may be compacted around an anode lead, which may be in the form of a wire, sheet, etc. The lead may extend in a longitudinal direction from the anode body and may be formed from any electrically conductive material, such as tantalum, niobium, aluminum, hafnium, titanium, etc., as well as electrically conductive oxides and/or nitrides of thereof. Connection of the lead to the anode body may also be accomplished using other known techniques, such as by welding the lead to the body or embedding it within the anode body during formation (e.g., prior to compaction and/or sintering).

Any binder may be removed after pressing by heating the pellet under vacuum at a certain temperature (e.g., from about 150°C to about 500°C) for several minutes. Alternatively, the binder may also be removed by contacting the pellet with an aqueous solution, such as described in U.S. Patent No. 6,197,252 to Bishop, et al. Thereafter, the pellet is sintered to form a porous, integral mass. The pellet is typically sintered at a temperature of from about 700°C to about 1800°C, in some embodiments from about 800°C to about 1700°C, and in some embodiments, from about 900°C to about 1400°C, for a time of from about 5 minutes to about 100 minutes, and in some embodiments, from about 8 minutes to about 15 minutes. This may occur in one or more steps. If desired, sintering may occur in an atmosphere that limits the transfer of oxygen atoms to the anode. For

example, sintering may occur in a reducing atmosphere, such as in a vacuum, inert gas, hydrogen, etc. The reducing atmosphere may be at a pressure of from about 10 Torr to about 2000 Torr, in some embodiments from about 100 Torr to about 1000 Torr, and in some embodiments, from about 100 Torr to about 930 Torr. Mixtures of hydrogen and other gases (e.g., argon or nitrogen) may also be employed.

B. Dielectric

The anode is also coated with a dielectric. The dielectric may be formed by anodically oxidizing ("anodizing") the sintered anode so that a dielectric layer is formed over and/or within the anode. For example, a tantalum (Ta) anode may be anodized to tantalum pentoxide (Ta_2O_5). Typically, anodization is performed by initially applying a solution to the anode, such as by dipping anode into the electrolyte. A solvent is generally employed, such as water (e.g., deionized water). To enhance ionic conductivity, a compound may be employed that is capable of dissociating in the solvent to form ions. Examples of such compounds include, for instance, acids, such as described below with respect to the electrolyte. For example, an acid (e.g., phosphoric acid) may constitute from about 0.01 wt.% to about 5 wt.%, in some embodiments from about 0.05 wt.% to about 0.8 wt.%, and in some embodiments, from about 0.1 wt.% to about 0.5 wt.% of the anodizing solution. If desired, blends of acids may also be employed.

A current is passed through the anodizing solution to form the dielectric layer. The value of the formation voltage manages the thickness of the dielectric layer. For example, the power supply may be initially set up at a galvanostatic mode until the required voltage is reached. Thereafter, the power supply may be switched to a potentiostatic mode to ensure that the desired dielectric thickness is formed over the entire surface of the anode. Of course, other known methods may also be employed, such as pulse or step potentiostatic methods. The voltage at which anodic oxidation occurs typically ranges from about 4 to about 250 V, and in some embodiments, from about 5 to about 200 V, and in some embodiments, from about 10 to about 150 V. During oxidation, the anodizing solution can be kept at an elevated temperature, such as about 30°C or more, in some embodiments from about 40°C to about 200°C, and in some embodiments, from about 50°C to about 100°C. Anodic oxidation can also be done at ambient temperature or lower. The

resulting dielectric layer may be formed on a surface of the anode and within its pores.

Although not required, in certain embodiments, the dielectric layer may possess a differential thickness throughout the anode in that it possesses a first portion that overlies an external surface of the anode and a second portion that overlies an interior surface of the anode. In such embodiments, the first portion is selectively formed so that its thickness is greater than that of the second portion. It should be understood, however, that the thickness of the dielectric layer need not be uniform within a particular region. Certain portions of the dielectric layer adjacent to the external surface may, for example, actually be thinner than certain portions of the layer at the interior surface, and vice versa. Nevertheless, the dielectric layer may be formed such that at least a portion of the layer at the external surface has a greater thickness than at least a portion at the interior surface. Although the exact difference in these thicknesses may vary depending on the particular application, the ratio of the thickness of the first portion to the thickness of the second portion is typically from about 1.2 to about 40, in some embodiments from about 1.5 to about 25, and in some embodiments, from about 2 to about 20.

To form a dielectric layer having a differential thickness, a multi-stage process is generally employed. In each stage of the process, the sintered anode is anodically oxidized (“anodized”) to form a dielectric layer (e.g., tantalum pentoxide). During the first stage of anodization, a relatively small forming voltage is typically employed to ensure that the desired dielectric thickness is achieved for the inner region, such as forming voltages ranging from about 1 to about 90 volts, in some embodiments from about 2 to about 50 volts, and in some embodiments, from about 5 to about 20 volts. Thereafter, the sintered body may then be anodically oxidized in a second stage of the process to increase the thickness of the dielectric to the desired level. This is generally accomplished by anodizing in an electrolyte at a higher voltage than employed during the first stage, such as at forming voltages ranging from about 50 to about 350 volts, in some embodiments from about 60 to about 300 volts, and in some embodiments, from about 70 to about 200 volts. During the first and/or second stages, the electrolyte may be kept at a temperature within the range of from about 15°C to about 95°C, in some

embodiments from about 20°C to about 90°C, and in some embodiments, from about 25°C to about 85°C.

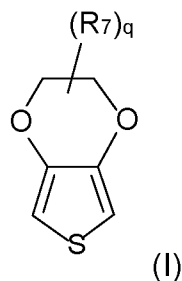
The electrolytes employed during the first and second stages of the anodization process may be the same or different. Typically, however, it is desired to employ different solutions to help better facilitate the attainment of a higher thickness at the outer portions of the dielectric layer. For example, it may be desired that the electrolyte employed in the second stage has a lower ionic conductivity than the electrolyte employed in the first stage to prevent a significant amount of oxide film from forming on the internal surface of anode. In this regard, the electrolyte employed during the first stage may contain an acidic compound, such as nitric acid, sulfuric acid, phosphoric acid, polyphosphoric acid, boric acid, boronic acid, etc. Such an electrolyte may have an electrical conductivity of from about 0.1 to about 100 mS/cm, in some embodiments from about 0.2 to about 20 mS/cm, and in some embodiments, from about 1 to about 10 mS/cm, determined at a temperature of 25°C. The electrolyte employed during the second stage typically contains a salt of a weak acid so that the hydronium ion concentration increases in the pores as a result of charge passage therein. Ion transport or diffusion is such that the weak acid anion moves into the pores as necessary to balance the electrical charges. As a result, the concentration of the principal conducting species (hydronium ion) is reduced in the establishment of equilibrium between the hydronium ion, acid anion, and undissociated acid, thus forms a poorer-conducting species. The reduction in the concentration of the conducting species results in a relatively high voltage drop in the electrolyte, which hinders further anodization in the interior while a thicker oxide layer, is being built up on the outside to a higher formation voltage in the region of continued high conductivity. Suitable weak acid salts may include, for instance, ammonium or alkali metal salts (e.g., sodium, potassium, etc.) of boric acid, boronic acid, acetic acid, oxalic acid, lactic acid, adipic acid, etc. Particularly suitable salts include sodium tetraborate and ammonium pentaborate. Such electrolytes typically have an electrical conductivity of from about 0.1 to about 20 mS/cm, in some embodiments from about 0.5 to about 10 mS/cm, and in some embodiments, from about 1 to about 5 mS/cm, determined at a temperature of 25°C.

If desired, each stage of anodization may be repeated for one or more cycles to achieve the desired dielectric thickness. Furthermore, the anode may also be rinsed or washed with another solvent (e.g., water) after the first and/or second stages to remove the electrolyte.

5 C. Solid Electrolyte

A solid electrolyte overlies the dielectric and generally functions as the cathode for the capacitor. The solid electrolyte may include materials as is known in the art, such as conductive polymers (e.g., polypyrroles, polythiophenes, polyanilines, etc.), manganese dioxide, and so forth. In one
10 embodiment, for example, the solid electrolyte contains one or more layers containing extrinsically and/or intrinsically conductive polymer particles. One benefit of employing such particles is that they can minimize the presence of ionic species (e.g., Fe^{2+} or Fe^{3+}) produced during conventional in situ polymerization processes, which can cause dielectric breakdown under high electric field due to
15 ionic migration. Thus, by applying the conductive polymer as pre-polymerized particles rather than through in situ polymerization, the resulting capacitor may exhibit a relatively high “breakdown voltage.” If desired, the solid electrolyte may be formed from one or multiple layers. When multiple layers are employed, it is possible that one or more of the layers includes a conductive polymer formed by in situ
20 polymerization. However, when it is desired to achieve very high breakdown voltages, the solid electrolyte may desirably be formed primarily from the conductive particles described above, such that it is generally free of conductive polymers formed via in situ polymerization. Regardless of the number of layers employed, the resulting solid electrolyte typically has a total thickness of from
25 about 1 micrometer (μm) to about 200 μm , in some embodiments from about 2 μm to about 50 μm , and in some embodiments, from about 5 μm to about 30 μm .

Thiophene polymers are particularly suitable for use in the solid electrolyte. In certain embodiments, for instance, an “extrinsically” conductive thiophene polymer may be employed in the solid electrolyte that has repeating
30 units of the following formula (I):



wherein,

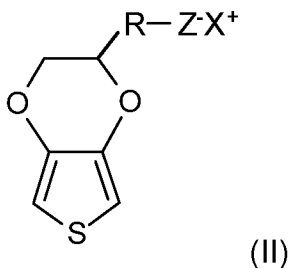
R_7 is a linear or branched, C_1 to C_{18} alkyl radical (e.g., methyl, ethyl, n- or iso-propyl, n-, iso-, sec- or tert-butyl, n-pentyl, 1-methylbutyl, 2-methylbutyl, 3-
 5 methylbutyl, 1-ethylpropyl, 1,1-dimethylpropyl, 1,2-dimethylpropyl, 2,2-
 dimethylpropyl, n-hexyl, n-heptyl, n-octyl, 2-ethylhexyl, n-nonyl, n-decyl, n-undecyl, n-dodecyl, n-tridecyl, n-tetradecyl, n-hexadecyl, n-octadecyl, etc.); C_5 to C_{12}
 cycloalkyl radical (e.g., cyclopentyl, cyclohexyl, cycloheptyl, cyclooctyl, cyclononyl, cyclodecyl, etc.); C_6 to C_{14} aryl radical (e.g., phenyl, naphthyl, etc.); C_7 to C_{18}
 10 aralkyl radical (e.g., benzyl, o-, m-, p-tolyl, 2,3-, 2,4-, 2,5-, 2,6-, 3,4-, 3,5-xylyl, mesityl, etc.); and

q is an integer from 0 to 8, in some embodiments, from 0 to 2, and in one
 embodiment, 0. In one particular embodiment, “ q ” is 0 and the polymer is poly(3,4-
 ethylenedioxythiophene). One commercially suitable example of a monomer
 15 suitable for forming such a polymer is 3,4-ethylenedioxythiophene, which is
 available from Heraeus under the designation Clevios™ M.

The polymers of formula (I) are generally considered to be “extrinsically”
 conductive to the extent that they typically require the presence of a separate
 counterion that is not covalently bound to the polymer. The counterion may be a
 20 monomeric or polymeric anion that counteracts the charge of the conductive
 polymer. Polymeric anions can, for example, be anions of polymeric carboxylic
 acids (e.g., polyacrylic acids, polymethacrylic acid, polymaleic acids, etc.);
 polymeric sulfonic acids (e.g., polystyrene sulfonic acids (“PSS”), polyvinyl sulfonic
 acids, etc.); and so forth. The acids may also be copolymers, such as copolymers
 25 of vinyl carboxylic and vinyl sulfonic acids with other polymerizable monomers,
 such as acrylic acid esters and styrene. Likewise, suitable monomeric anions
 include, for example, anions of C_1 to C_{20} alkane sulfonic acids (e.g., dodecane
 sulfonic acid); aliphatic perfluorosulfonic acids (e.g., trifluoromethane sulfonic acid,

perfluorobutane sulfonic acid or perfluorooctane sulfonic acid); aliphatic C₁ to C₂₀ carboxylic acids (e.g., 2-ethyl-hexylcarboxylic acid); aliphatic perfluorocarboxylic acids (e.g., trifluoroacetic acid or perfluorooctanoic acid); aromatic sulfonic acids optionally substituted by C₁ to C₂₀ alkyl groups (e.g., benzene sulfonic acid, o-toluene sulfonic acid, p-toluene sulfonic acid or dodecylbenzene sulfonic acid);
 5 cycloalkane sulfonic acids (e.g., camphor sulfonic acid or tetrafluoroborates, hexafluorophosphates, perchlorates, hexafluoroantimonates, hexafluoroarsenates or hexachloroantimonates); and so forth. Particularly suitable counteranions are polymeric anions, such as a polymeric carboxylic or sulfonic acid (e.g., polystyrene sulfonic acid ("PSS")). The molecular weight of such polymeric anions typically
 10 ranges from about 1,000 to about 2,000,000, and in some embodiments, from about 2,000 to about 500,000.

Intrinsically conductive polymers may also be employed that have a positive charge located on the main chain that is at least partially compensated by anions
 15 covalently bound to the polymer. For example, one example of a suitable intrinsically conductive thiophene polymer may have repeating units of the following formula (II):



wherein,

20 R is (CH₂)_a-O-(CH₂)_b-L, where L is a bond or HC([CH₂)_cH);

a is from 0 to 10, in some embodiments from 0 to 6, and in some embodiments, from 1 to 4 (e.g., 1);

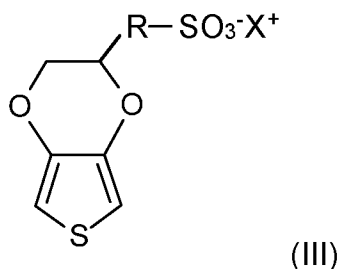
b is from 1 to 18, in some embodiments from 1 to 10, and in some embodiments, from 2 to 6 (e.g., 2, 3, 4, or 5);

25 c is from 0 to 10, in some embodiments from 0 to 6, and in some embodiments, from 1 to 4 (e.g., 1);

Z is an anion, such as SO₃⁻, C(O)O⁻, BF₄⁻, CF₃SO₃⁻, SbF₆⁻, N(SO₂CF₃)₂⁻, C₄H₃O₄⁻, ClO₄⁻, etc.; and

X is a cation, such as hydrogen, an alkali metal (e.g., lithium, sodium, rubidium, cesium or potassium), ammonium, etc.

In one particular embodiment, Z in formula (II) is a sulfonate ion such that the intrinsically conductive polymer contains repeating units of the following
5 formula (III):



wherein, R and X are defined above. In formula (II) or (III), a is preferably 1 and b is preferably 3 or 4. Likewise, X is preferably sodium or potassium.

If desired, the polymer may be a copolymer that contains other types of
10 repeating units. In such embodiments, the repeating units of formula (II) typically constitute about 50 mol.% or more, in some embodiments from about 75 mol.% to about 99 mol.%, and in some embodiments, from about 85 mol.% to about 95 mol.% of the total amount of repeating units in the copolymer. Of course, the polymer may also be a homopolymer to the extent that it contains 100 mol.% of
15 the repeating units of formula (II). Specific examples of such homopolymers include poly(4-(2,3-dihydrothieno-[3,4-b][1,4]dioxin-2-ylmethoxy)-1-butane-sulphonic acid, salt) and poly(4-(2,3-dihydrothieno-[3,4-b][1,4]dioxin-2-ylmethoxy)-1-propanesulphonic acid, salt).

Regardless of the particular nature of the polymer, the resulting conductive
20 polymer particles typically have an average size (e.g., diameter) of from about 1 to about 80 nanometers, in some embodiments from about 2 to about 70 nanometers, and in some embodiments, from about 3 to about 60 nanometers. The diameter of the particles may be determined using known techniques, such as by ultracentrifuge, laser diffraction, etc. The shape of the particles may likewise
25 vary. In one particular embodiment, for instance, the particles are spherical in shape. However, it should be understood that other shapes are also contemplated by the present invention, such as plates, rods, discs, bars, tubes, irregular shapes, etc.

Although not necessarily required, the conductive polymer particles may be

applied in the form of a dispersion. The concentration of the conductive polymer in the dispersion may vary depending on the desired viscosity of the dispersion and the particular manner in which the dispersion is to be applied to the capacitor element. Typically, however, the polymer constitutes from about 0.1 to about 10 wt.%, in some embodiments from about 0.4 to about 5 wt.%, and in some 5 embodiments, from about 0.5 to about 4 wt.% of the dispersion. The dispersion may also contain one or more components to enhance the overall properties of the resulting solid electrolyte. For example, the dispersion may contain a binder to further enhance the adhesive nature of the polymeric layer and also increase the 10 stability of the particles within the dispersion. The binder may be organic in nature, such as polyvinyl alcohols, polyvinyl pyrrolidones, polyvinyl chlorides, polyvinyl acetates, polyvinyl butyrates, polyacrylic acid esters, polyacrylic acid amides, polymethacrylic acid esters, polymethacrylic acid amides, polyacrylonitriles, styrene/acrylic acid ester, vinyl acetate/acrylic acid ester and ethylene/vinyl acetate 15 copolymers, polybutadienes, polyisoprenes, polystyrenes, polyethers, polyesters, polycarbonates, polyurethanes, polyamides, polyimides, polysulfones, melamine formaldehyde resins, epoxide resins, silicone resins or celluloses. Crosslinking agents may also be employed to enhance the adhesion capacity of the binders. Such crosslinking agents may include, for instance, melamine compounds, 20 masked isocyanates or crosslinkable polymers, such as polyurethanes, polyacrylates or polyolefins, and subsequent crosslinking. Dispersion agents may also be employed to facilitate the ability to apply the layer to the anode. Suitable dispersion agents include solvents, such as aliphatic alcohols (e.g., methanol, ethanol, i-propanol and butanol), aliphatic ketones (e.g., acetone and methyl ethyl 25 ketones), aliphatic carboxylic acid esters (e.g., ethyl acetate and butyl acetate), aromatic hydrocarbons (e.g., toluene and xylene), aliphatic hydrocarbons (e.g., hexane, heptane and cyclohexane), chlorinated hydrocarbons (e.g., dichloromethane and dichloroethane), aliphatic nitriles (e.g., acetonitrile), aliphatic sulfoxides and sulfones (e.g., dimethyl sulfoxide and sulfolane), aliphatic carboxylic 30 acid amides (e.g., methylacetamide, dimethylacetamide and dimethylformamide), aliphatic and araliphatic ethers (e.g., diethylether and anisole), water, and mixtures of any of the foregoing solvents. A particularly suitable dispersion agent is water.

In addition to those mentioned above, still other ingredients may also be

used in the dispersion. For example, conventional fillers may be used that have a size of from about 10 nanometers to about 100 micrometers, in some embodiments from about 50 nanometers to about 50 micrometers, and in some embodiments, from about 100 nanometers to about 30 micrometers. Examples of
5 such fillers include calcium carbonate, silicates, silica, calcium or barium sulfate, aluminum hydroxide, glass fibers or bulbs, wood flour, cellulose powder carbon black, electrically conductive polymers, etc. The fillers may be introduced into the dispersion in powder form, but may also be present in another form, such as fibers.

Surface-active substances may also be employed in the dispersion, such as
10 ionic or non-ionic surfactants. Furthermore, adhesives may be employed, such as organofunctional silanes or their hydrolysates, for example 3-glycidoxypropyltrialkoxysilane, 3-aminopropyl-triethoxysilane, 3-mercaptopropyl-trimethoxysilane, 3-metacryloxypropyltrimethoxysilane, vinyltrimethoxysilane or octyltriethoxysilane. The dispersion may also contain additives that increase
15 conductivity, such as ether group-containing compounds (e.g., tetrahydrofuran), lactone group-containing compounds (e.g., γ -butyrolactone or γ -valerolactone), amide or lactam group-containing compounds (e.g., caprolactam, N-methylcaprolactam, N,N-dimethylacetamide, N-methylacetamide, N,N-dimethylformamide (DMF), N-methylformamide, N-methylformanilide, N-
20 methylpyrrolidone (NMP), N-octylpyrrolidone, or pyrrolidone), sulfones and sulfoxides (e.g., sulfolane (tetramethylenesulfone) or dimethylsulfoxide (DMSO)), sugar or sugar derivatives (e.g., saccharose, glucose, fructose, or lactose), sugar alcohols (e.g., sorbitol or mannitol), furan derivatives (e.g., 2-furancarboxylic acid or 3-furancarboxylic acid), an alcohols (e.g., ethylene glycol, glycerol, di- or
25 triethylene glycol).

The dispersion may be applied using a variety of known techniques, such as by spin coating, impregnation, pouring, dropwise application, injection, spraying, doctor blading, brushing, printing (e.g., ink-jet, screen, or pad printing), or dipping. The viscosity of the dispersion is typically from about 0.1 to about 100,000 mPas
30 (measured at a shear rate of 100 s^{-1}), in some embodiments from about 1 to about 10,000 mPas, in some embodiments from about 10 to about 1,500 mPas, and in some embodiments, from about 100 to about 1000 mPas.

i. Inner Layers

The solid electrolyte is generally formed from one or more “inner”
conductive polymer layers. The term “inner” in this context refers to one or more
layers that overly the dielectric, whether directly or via another layer (e.g., pre-
coat layer). One or multiple inner layers may be employed. For example, the
5 solid electrolyte typically contains from 2 to 30, in some embodiments from 4 to
20, and in some embodiments, from about 5 to 15 inner layers (e.g., 10 layers).
The inner layer(s) may, for example, contain intrinsically and/or extrinsically
conductive polymer particles such as described above. For instance, such
particles may constitute about 50 wt.% or more, in some embodiments about 70
10 wt.% or more, and in some embodiments, about 90 wt.% or more (e.g., 100
wt.%) of the inner layer(s). In alternative embodiments, the inner layer(s) may
contain an in-situ polymerized conductive polymer. In such embodiments, the in-
situ polymerized polymers may constitute about 50 wt.% or more, in some
embodiments about 70 wt.% or more, and in some embodiments, about 90 wt.%
15 or more (e.g., 100 wt.%) of the inner layer(s).

ii. Outer Layers

The solid electrolyte may also contain one or more optional “outer”
conductive polymer layers that overly the inner layer(s) and are formed from a
different material. For example, the outer layer(s) may contain extrinsically
20 conductive polymer particles. In one particular embodiment, the outer layer(s)
are formed primarily from such extrinsically conductive polymer particles in that
they constitute about 50 wt.% or more, in some embodiments about 70 wt.% or
more, and in some embodiments, about 90 wt.% or more (e.g., 100 wt.%) of a
respective outer layer. One or multiple outer layers may be employed. For
25 example, the solid electrolyte may contain from 2 to 30, in some embodiments
from 4 to 20, and in some embodiments, from about 5 to 15 outer layers, each of
which may optionally be formed from a dispersion of the extrinsically conductive
polymer particles.

D. External Polymer Coating

30 An external polymer coating may also overly the solid electrolyte. The
external polymer coating may contain one or more layers formed from pre-
polymerized conductive polymer particles such as described above (e.g.,
dispersion of extrinsically conductive polymer particles). The external coating may

be able to further penetrate into the edge region of the capacitor body to increase the adhesion to the dielectric and result in a more mechanically robust part, which may reduce equivalent series resistance and leakage current. Because it is generally intended to improve the degree of edge coverage rather to impregnate the interior of the anode body, the particles used in the external coating typically have a larger size than those employed in the solid electrolyte. For example, the ratio of the average size of the particles employed in the external polymer coating to the average size of the particles employed in any dispersion of the solid electrolyte is typically from about 1.5 to about 30, in some embodiments from about 2 to about 20, and in some embodiments, from about 5 to about 15. For example, the particles employed in the dispersion of the external coating may have an average size of from about 80 to about 500 nanometers, in some embodiments from about 90 to about 250 nanometers, and in some embodiments, from about 100 to about 200 nanometers.

If desired, a crosslinking agent may also be employed in the external polymer coating to enhance the degree of adhesion to the solid electrolyte. Typically, the crosslinking agent is applied prior to application of the dispersion used in the external coating. Suitable crosslinking agents are described, for instance, in U.S. Patent Publication No. 2007/0064376 to Merker, et al. and include, for instance, amines (e.g., diamines, triamines, oligomer amines, polyamines, etc.); polyvalent metal cations, such as salts or compounds of Mg, Al, Ca, Fe, Cr, Mn, Ba, Ti, Co, Ni, Cu, Ru, Ce or Zn, phosphonium compounds, sulfonium compounds, etc. Particularly suitable examples include, for instance, 1,4-diaminocyclohexane, 1,4-bis(amino-methyl)cyclohexane, ethylenediamine, 1,6-hexanediamine, 1,7-heptanediamine, 1,8-octanediamine, 1,9-nonanediamine, 1,10-decanediamine, 1,12-dodecanediamine, N,N-dimethylethylenediamine, N,N,N',N'-tetramethylethylenediamine, N,N,N',N'-tetramethyl-1,4-butanediamine, etc., as well as mixtures thereof.

The crosslinking agent is typically applied from a solution or dispersion whose pH is from 1 to 10, in some embodiments from 2 to 7, in some embodiments, from 3 to 6, as determined at 25°C. Acidic compounds may be employed to help achieve the desired pH level. Examples of solvents or dispersants for the crosslinking agent include water or organic solvents, such as

alcohols, ketones, carboxylic esters, etc. The crosslinking agent may be applied to the capacitor body by any known process, such as spin-coating, impregnation, casting, dropwise application, spray application, vapor deposition, sputtering, sublimation, knife-coating, painting or printing, for example inkjet, screen or pad printing. Once applied, the crosslinking agent may be dried prior to application of the polymer dispersion. This process may then be repeated until the desired thickness is achieved. For example, the total thickness of the entire external polymer coating, including the crosslinking agent and dispersion layers, may range from about 1 to about 50 μm , in some embodiments from about 2 to about 40 μm , and in some embodiments, from about 5 to about 20 μm .

E. Cathode Coating

If desired, the capacitor element may also employ a cathode coating that overlies the solid electrolyte and other optional layers (e.g., external polymer coating). The cathode coating may contain a metal particle layer includes a plurality of conductive metal particles dispersed within a polymer matrix. The particles typically constitute from about 50 wt.% to about 99 wt.%, in some embodiments from about 60 wt.% to about 98 wt.%, and in some embodiments, from about 70 wt.% to about 95 wt.% of the layer, while the polymer matrix typically constitutes from about 1 wt.% to about 50 wt.%, in some embodiments from about 2 wt.% to about 40 wt.%, and in some embodiments, from about 5 wt.% to about 30 wt.% of the layer.

The conductive metal particles may be formed from a variety of different metals, such as copper, nickel, silver, nickel, zinc, tin, lead, copper, aluminum, molybdenum, titanium, iron, zirconium, magnesium, etc., as well as alloys thereof. Silver is a particularly suitable conductive metal for use in the layer. The metal particles often have a relatively small size, such as an average size of from about 0.01 to about 50 micrometers, in some embodiments from about 0.1 to about 40 micrometers, and in some embodiments, from about 1 to about 30 micrometers. Typically, only one metal particle layer is employed, although it should be understood that multiple layers may be employed if so desired. The total thickness of such layer(s) is typically within the range of from about 1 μm to about 500 μm , in some embodiments from about 5 μm to about 200 μm , and in some embodiments, from about 10 μm to about 100 μm .

The polymer matrix typically includes a polymer, which may be thermoplastic or thermosetting in nature. Typically, however, the polymer is selected so that it can act as a barrier to electromigration of silver ions, and also so that it contains a relatively small amount of polar groups to minimize the degree of water adsorption in the cathode coating. In this regard, the present inventors have found that vinyl acetal polymers are particularly suitable for this purpose, such as polyvinyl butyral, polyvinyl formal, etc. Polyvinyl butyral, for instance, may be formed by reacting polyvinyl alcohol with an aldehyde (e.g., butyraldehyde). Because this reaction is not typically complete, polyvinyl butyral will generally have a residual hydroxyl content. By minimizing this content, however, the polymer can possess a lesser degree of strong polar groups, which would otherwise result in a high degree of moisture adsorption and result in silver ion migration. For instance, the residual hydroxyl content in polyvinyl acetal may be about 35 mol.% or less, in some embodiments about 30 mol.% or less, and in some embodiments, from about 10 mol.% to about 25 mol.%. One commercially available example of such a polymer is available from Sekisui Chemical Co., Ltd. under the designation "BH-S" (polyvinyl butyral).

To form the cathode coating, a conductive paste is typically applied to the capacitor that overlies the solid electrolyte. One or more organic solvents are generally employed in the paste. A variety of different organic solvents may generally be employed, such as glycols (e.g., propylene glycol, butylene glycol, triethylene glycol, hexylene glycol, polyethylene glycols, ethoxydiglycol, and dipropyleneglycol); glycol ethers (e.g., methyl glycol ether, ethyl glycol ether, and isopropyl glycol ether); ethers (e.g., diethyl ether and tetrahydrofuran); alcohols (e.g., benzyl alcohol, methanol, ethanol, n-propanol, iso-propanol, and butanol); triglycerides; ketones (e.g., acetone, methyl ethyl ketone, and methyl isobutyl ketone); esters (e.g., ethyl acetate, butyl acetate, diethylene glycol ether acetate, and methoxypropyl acetate); amides (e.g., dimethylformamide, dimethylacetamide, dimethylcaprylic/capric fatty acid amide and N-alkylpyrrolidones); nitriles (e.g., acetonitrile, propionitrile, butyronitrile and benzonitrile); sulfoxides or sulfones (e.g., dimethyl sulfoxide (DMSO) and sulfolane); etc., as well as mixtures thereof. The organic solvent(s) typically constitute from about 10 wt.% to about 70 wt.%, in some embodiments from about 20 wt.% to about 65 wt.%, and in some

embodiments, from about 30 wt.% to about 60 wt.% of the paste. Typically, the metal particles constitute from about 10 wt.% to about 60 wt.%, in some embodiments from about 20 wt.% to about 45 wt.%, and in some embodiments, from about 25 wt.% to about 40 wt.% of the paste, and the resinous matrix
5 constitutes from about 0.1 wt.% to about 20 wt.%, in some embodiments from about 0.2 wt.% to about 10 wt.%, and in some embodiments, from about 0.5 wt.% to about 8 wt.% of the paste.

The paste may have a relatively low viscosity, allowing it to be readily handled and applied to a capacitor element. The viscosity may, for instance,
10 range from about 50 to about 3,000 centipoise, in some embodiments from about 100 to about 2,000 centipoise, and in some embodiments, from about 200 to about 1,000 centipoise, such as measured with a Brookfield DV-1 viscometer (cone and plate) operating at a speed of 10 rpm and a temperature of 25°C. If desired, thickeners or other viscosity modifiers may be employed in the paste to increase or
15 decrease viscosity. Further, the thickness of the applied paste may also be relatively thin and still achieve the desired properties. For example, the thickness of the paste may be from about 0.01 to about 50 micrometers, in some embodiments from about 0.5 to about 30 micrometers, and in some embodiments, from about 1 to about 25 micrometers. Once applied, the metal paste may be
20 optionally dried to remove certain components, such as the organic solvents. For instance, drying may occur at a temperature of from about 20°C to about 150°C, in some embodiments from about 50°C to about 140°C, and in some embodiments, from about 80°C to about 130°C.

F. Other Components

25 If desired, the capacitor may also contain other layers as is known in the art. In certain embodiments, for instance, a carbon layer (e.g., graphite) may be positioned between the solid electrolyte and the silver layer that can help further limit contact of the silver layer with the solid electrolyte. In addition, a pre-coat layer may also be employed that overlies the dielectric and includes an
30 organometallic compound, such as described in more detail below.

II. Terminations

Once the desired layers are formed, the capacitor may be provided with terminations as indicated above. More particularly, the capacitor contains an anode termination to which an anode lead of the capacitor element is electrically
5 connected and a cathode termination to which the solid electrolyte of the capacitor element is electrically connected. Any conductive material may be employed to form the terminations, such as a conductive metal (e.g., copper, nickel, silver, nickel, zinc, tin, palladium, lead, copper, aluminum, molybdenum, titanium, iron, zirconium, magnesium, and alloys thereof). Particularly suitable conductive metals
10 include, for instance, copper, copper alloys (e.g., copper-zirconium, copper-magnesium, copper-zinc, or copper-iron), nickel, and nickel alloys (e.g., nickel-iron). The thickness of the terminations is generally selected to minimize the thickness of the capacitor. For instance, the thickness of the terminations may range from about 0.05 to about 1 millimeter, in some embodiments from about
15 0.05 to about 0.5 millimeters, and from about 0.07 to about 0.2 millimeters. One exemplary conductive material is a copper-iron alloy metal plate available from Wieland (Germany). If desired, the surface of the terminations may be electroplated with nickel, silver, gold, tin, etc. as is known in the art to ensure that the final part is mountable to the circuit board. In one particular embodiment, both
20 surfaces of the terminations are plated with nickel and silver flashes, respectively, while the mounting surface is also plated with a tin solder layer.

The terminations may be connected to the capacitor element using any technique known in the art. In one embodiment, for example, a lead frame may be provided that defines the cathode termination and anode termination. To attach
25 the capacitor element to the lead frame, a conductive adhesive may initially be applied to a surface of the cathode termination. The conductive adhesive may include, for instance, conductive metal particles contained with a resin composition. The metal particles may be silver, copper, gold, platinum, nickel, zinc, bismuth, etc. The resin composition may include a thermoset resin (e.g.,
30 epoxy resin), curing agent (e.g., acid anhydride), and coupling agent (e.g., silane coupling agents). Suitable conductive adhesives may be described in U.S. Patent Application Publication No. 2006/0038304 to Osako, et al. Any of a variety of techniques may be used to apply the conductive adhesive to the cathode

termination. Printing techniques, for instance, may be employed due to their practical and cost-saving benefits. The anode lead may also be electrically connected to the anode termination using any technique known in the art, such as mechanical welding, laser welding, conductive adhesives, etc. Upon electrically
5 connecting the anode lead to the anode termination, the conductive adhesive may then be cured to ensure that the electrolytic capacitor is adequately adhered to the cathode termination.

Referring to Fig. 1, for example, a capacitor 30 is shown that has a generally rectangular shape in that it extends in a longitudinal direction “x”,
10 transverse direction “y”, and vertical direction “z.” The capacitor 30 includes an anode termination 62 and a cathode termination 72 in electrical connection with a capacitor element 33 having an upper surface 37, a lower surface 39 opposing the upper surface 37, a front surface 36, a rear surface 38 opposing the front surface 36, a first side surface 35, and an opposing side surface (not shown). The
15 cathode termination 72 may be provided in electrical contact with any surface of the capacitor element, such as via a conductive adhesive. In the illustrated embodiment, for example, the cathode termination 72 contains a first component 73 that is generally parallel and adjacent to the upper surface 37 and a second component 75 that is generally parallel and adjacent to the lower surface 39. The
20 first component 73 is also in electrical contact with the upper surface 37. The cathode termination 72 may also contain a third component 77 generally extends in a direction perpendicular to the first component 73 and second component 75. If desired, the third component 77 may also be provided in electrical contact with the rear surface 38 of the capacitor element 33. The anode termination 62
25 likewise contains a first component 63 that is generally parallel to the lower surface 39 of the capacitor element 33 and a second component 67 that is generally parallel to the anode lead 16. Further, the anode termination 62 may include a third component 64 that is generally perpendicular to the first component 63 and a fourth component 69 that is generally perpendicular to the second component 67
30 and located adjacent to the anode lead 16.

The terminations may be connected to the capacitor element using any technique known in the art. In one embodiment, for example, a lead frame may be provided that defines the cathode termination 72 and anode termination 62. To

attach the capacitor element 33 to the lead frame, a conductive adhesive 49 may initially be applied to a surface of the cathode termination 72. In one embodiment, the anode termination 62 and cathode termination 72 are folded into the position shown in Fig. 1. Thereafter, the capacitor element 33 is positioned on the cathode termination 72 so that its lower surface 39 contacts the adhesive 49 and the anode lead 16 contacts the region 51. The anode lead 16 is then electrically connected to the region 51 using any technique known in the art, such as mechanical welding, laser welding, conductive adhesives, etc. For example, the anode lead 16 may be welded to the anode termination 62 using a laser. Lasers generally contain resonators that include a laser medium capable of releasing photons by stimulated emission and an energy source that excites the elements of the laser medium. One type of suitable laser is one in which the laser medium consists of an aluminum and yttrium garnet (YAG), doped with neodymium (Nd). The excited particles are neodymium ions Nd^{3+} . The energy source may provide continuous energy to the laser medium to emit a continuous laser beam or energy discharges to emit a pulsed laser beam. Upon electrically connecting the anode lead 16 to the anode termination 62, the conductive adhesive may then be cured. For example, a heat press may be used to apply heat and pressure to ensure that the electrolytic capacitor element 33 is adequately adhered to the cathode termination 72 by the adhesive 49.

In the illustrated embodiment, the second component 67 and fourth component 69 also define a connection region 51 at which the anode lead 16 is connected to the anode termination 62. Although not depicted in Fig. 1, the region 51 may possess a "U-shape" to further enhance surface contact and mechanical stability of the lead 16. As noted above, relative to the length of the capacitor, the distance between the connection region (e.g., where the anode lead contacts the anode termination) and the front surface of the capacitor element may be relatively large. In Fig. 1, for instance, the capacitor 30 is shown as having a length " L_2 " extending in the longitudinal direction "x." Likewise, Fig. 1 also illustrates the distance " L_1 " that spans from the front surface 36 of the capacitor element 33 to the connection region 51 at which the anode lead 16 is connected to the anode termination 62. The ratio of the distance " L_1 " to the length " L_2 " (i.e., L_1/L_2) is typically 0.13 or more, in some embodiments 0.14 or more, in some

embodiments about 0.15 or more, and in some embodiments, from 0.16 to 0.5. The distance “L₁”, for instance, typically ranges from about 1 to about 2 millimeters, in some embodiments from about 1 to about 1.8 millimeters, and in some embodiments, from about 1.1 to about 1.6 millimeters, while the length “L₂” typically ranges from about 1 to about 15 millimeters, in some embodiments from about 2 to about 15 millimeters, in some embodiments from about 2 to about 12 millimeters, and in some embodiments, from about 2 to about 8 millimeters.

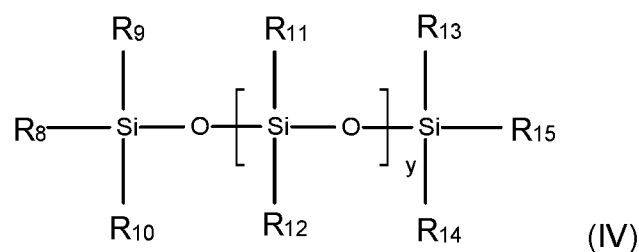
To help further minimize the likelihood of delamination, an interfacial coating is also employed that covers at least a portion of the anode termination and/or cathode termination and is in contact with the casing material. In contrast to the metal components commonly employed in the anode and cathode terminations, the interfacial coating may be formed from a resinous material that has a coefficient of thermal expansion similar in nature to the curable resinous matrix used in the casing material. Again, this can further reduce the likelihood that any expansion of the casing material during manufacturing will result in delamination from the anode lead and/or capacitor element.

One or multiple coatings may be employed. In one embodiment, for instance, an interfacial coating may be employed that covers at least a portion of the anode termination. In such embodiments, the coating may also contact at least a portion of a surface of the capacitor element, such as a front surface, bottom surface, and/or top surface of the capacitor element. Likewise, the coating may also contact at least a portion of the anode lead. In another embodiment, an interfacial coating may be employed that covers at least a portion of the cathode termination. In such embodiments, the coating may also contact at least a portion of a surface of the capacitor element, such as a rear surface, top surface, and/or bottom surface. Referring again to Fig. 1, for example, the capacitor 30 is shown with an interfacial coating 90 that is on the anode termination 62. More particularly, in the illustrated embodiment, the coating 90 is in contact with the second component 67 and the fourth component 69 of the anode termination 62 so that the region 51 is generally covered. The coating 90 is also in contact with at least a portion of the anode lead 16, particularly at those locations surrounding the region 51 at which the lead 16 is connected to the anode termination 62. Of course, it should be understood that the coating may also be provided in other

configurations and disposed on any surface desired. In one embodiment, for example, the coating may contact only the second component 67 of the anode termination 62.

Regardless of where it is located, the resinous material employed in the interfacial coating may be selectively controlled to impart certain desired properties to the resulting capacitor. In one embodiment, for instance, the interfacial coating may include a hydrophobic resinous material. The interfacial coating may exhibit a high degree of adhesion strength to the casing material, which makes it less likely to delaminate from the capacitor element when exposed to the high temperatures often experienced during manufacturing of the capacitor (e.g., reflow). Suitable hydrophobic resinous materials may include low surface energy polymers (e.g., fluoropolymer, silicone, etc.), organometallic compounds, etc. Fluoropolymers, for instance, may contain a hydrocarbon backbone polymer (e.g., polyolefin) in which some or all of the hydrogen atoms are substituted with fluorine groups, such as fluoroalkyl groups (e.g., trifluoromethyl, trifluoroethyl, etc.). The backbone polymer may likewise be formed from ethylenically unsaturated monomers (e.g., olefins, olefinic acrylates, olefinic methacrylates, etc.). Suitable monomers may, for instance, have a carbon chain length of from 3 to 20 atoms, in some embodiments from 6 to 12 carbon atoms in length, and in some embodiments, from 8 to 10 carbon atoms in length. Particularly suitable fluoroalkyl-substituted monomers for use in the present invention are fluoroalkyl (meth)acrylates, such as perfluorohexyl (meth)acrylate, perfluoroheptyl (meth)acrylate, perfluorooctyl (meth)acrylate, perfluorononyl perfluorodecyl (meth)acrylate, perfluoroundecyl (meth)acrylate or perfluorododecyl (meth)acrylate, etc., as well as mixtures thereof. As used herein, the term “(meth)acrylic” includes both acrylate and methacrylate monomers.

Another suitable low surface energy polymer that may be employed is a silicone polymer. Such polymers are typically derived from polyorganosiloxanes, such as those having the following general formula (IV):

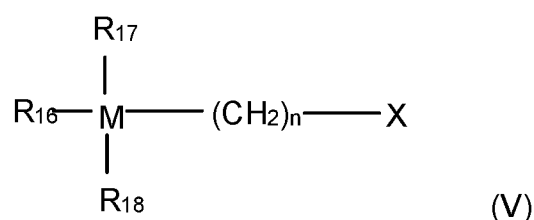


wherein,

y is an integer greater than 1; and

R₈, R₉, R₁₀, R₁₁, R₁₂, R₁₃, R₁₄, and R₁₅ are independently monovalent groups typically containing from 1 to about 20 carbon atoms, such as alkyl groups (e.g., methyl, ethyl, propyl, pentyl, octyl, undecyl, octadecyl, etc.); alkoxy groups (e.g., methoxy, ethoxy, propoxy, etc.); carboxyalkyl groups (e.g., acetyl); cycloalkyl groups (e.g., cyclohexyl); alkenyl groups (e.g., vinyl, allyl, butenyl, hexenyl, etc.); aryl groups (e.g., phenyl, tolyl, xylyl, benzyl, 2-phenylethyl, etc.); and halogenated hydrocarbon groups (e.g., 3,3,3-trifluoropropyl, 3-chloropropyl, dichlorophenyl, etc.). Examples of such polyorganosiloxanes may include, for instance, polydimethylsiloxane ("PDMS"), polymethylhydrogensiloxane, dimethyldiphenylpolysiloxane, dimethyl/methylphenylpolysiloxane, polymethylphenylsiloxane, methylphenyl/dimethylsiloxane, vinyl dimethyl terminated polydimethylsiloxane, vinylmethyl/dimethylpolysiloxane, vinyl dimethyl terminated vinylmethyl/dimethylpolysiloxane, divinylmethyl terminated polydimethylsiloxane, vinylphenylmethyl terminated polydimethylsiloxane, dimethylhydro terminated polydimethylsiloxane, methylhydro/dimethylpolysiloxane, methylhydro terminated methyloctylpolysiloxane, methylhydro/phenylmethyl polysiloxane, fluoro-modified polysiloxane, etc. To form the hydrophobic material, the polyorganosiloxane may be crosslinked using any of a variety of known techniques, such as by catalyst curing (e.g., platinum catalysts), room temperature vulcanization, moisture curing, etc. Crosslinking agents may be employed, such as alkoxy silanes having the formula Si-OR, wherein R is H, alkyl (e.g., methyl), alkenyl, carboxyalkyl (e.g., acetyl), and so forth.

Of course, still other hydrophobic materials may also be employed in the interfacial coating. In one embodiment, for instance, the hydrophobic material may include an organometallic compound, such as those having the following general formula (V):



wherein,

M is an organometallic atom, such as silicon, titanium, and so forth;

R₁₆, R₁₇, and R₁₈ are independently an alkyl (e.g., methyl, ethyl, propyl, etc.) or a hydroxyalkyl (e.g., hydroxymethyl, hydroxyethyl, hydroxypropyl, etc.), wherein at least one of R₁₆, R₁₇, and R₁₈ is a hydroxyalkyl;

5 n is an integer from 0 to 8, in some embodiments from 1 to 6, and in some embodiments, from 2 to 4 (e.g., 3); and

X is an organic or inorganic functional group, such as glycidyl, glycidyloxy, mercapto, amino, vinyl, etc.

In certain embodiments, R₁₆, R₁₇, and R₁₈ may a hydroxyalkyl (e.g., OCH₃).

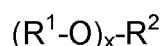
10 In other embodiments, however, R₁₆ may be an alkyl (e.g., CH₃) and R₁₇ and R₁₈ may a hydroxyalkyl (e.g., OCH₃).

In certain embodiments, M may be silicon so that the organometallic compound is an organosilane compound, such as an alkoxy silane. Suitable alkoxy silanes may include, for instance, 3-aminopropyltrimethoxysilane, 3-aminopropyltriethoxysilane, 3-aminopropylmethyldimethoxysilane, 3-aminopropylmethyldiethoxysilane, 3-(2-aminoethyl)aminopropyltrimethoxysilane, 3-mercaptopropyltrimethoxysilane, 3-mercaptopropyltriethoxysilane, 3-mercaptopropylmethyldimethoxysilane, 3-mercaptopropylmethyldiethoxysilane, glycidoxymethyltrimethoxysilane, glycidoxymethyltriethoxysilane, glycidoxymethyl-
 15 tripropoxysilane, glycidoxymethyltributoxysilane, β-glycidoxyethyltrimethoxysilane, β-glycidoxyethyltriethoxysilane, β-glycidoxyethyl-tripropoxysilane, β-glycidoxyethyl-tributoxysilane, β-glycidoxyethyltrimethoxysilane, α-glycidoxyethyltriethoxysilane, α-glycidoxyethyltripropoxysilane, α-glycidoxyethyltributoxysilane, γ-glycidoxypropyl-trimethoxysilane, γ-glycidoxypropyltriethoxysilane, γ-glycidoxypropyl-tripropoxysilane, γ-glycidoxypropyltributoxysilane, β-glycidoxypropyltrimethoxysilane, β-glycidoxypropyl-triethoxysilane, β-glycidoxypropyltripropoxysilane, α-glycidoxypropyltributoxysilane, α-glycidoxypropyltrimethoxysilane, α-glycidoxypropyltriethoxysilane, α-glycidoxypropyl-tripropoxysilane, α-glycidoxypropyltributoxysilane, γ-glycidoxybutyltrimethoxysilane, δ-glycidoxybutyltriethoxysilane, δ-glycidoxybutyltripropoxysilane, δ-glycidoxybutyl-tributoxysilane, δ-glycidoxybutyltrimethoxysilane, γ-glycidoxybutyltriethoxysilane, γ-

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glycidoxybutyltripropoxysilane, γ -propoxybutyltributoxysilane, δ -glycidoxybutyl-trimethoxysilane, δ -glycidoxybutyltriethoxysilane, δ -glycidoxybutyltripropoxysilane, α -glycidoxybutyltrimethoxysilane, α -glycidoxybutyltriethoxysilane, α -glycidoxybutyl-tripropoxysilane, α -glycidoxybutyltributoxysilane, (3,4-epoxycyclohexyl)-methyl-
 5 trimethoxysilane, (3,4-epoxycyclohexyl)methyl-triethoxysilane, (3,4-epoxycyclohexyl)methyltripropoxysilane, (3,4-epoxycyclohexyl)-methyl-tributoxysilane, (3,4-epoxycyclohexyl)ethyl-trimethoxysilane, (3,4-epoxycyclohexyl)ethyl-triethoxysilane, (3,4-epoxycyclohexyl)ethyltripropoxysilane, (3,4-epoxycyclohexyl)ethyltributoxysilane, (3,4-
 10 epoxycyclohexyl)propyltrimethoxysilane, (3,4-epoxycyclohexyl)propyltriethoxysilane, (3,4-epoxycyclohexyl)propyltripropoxysilane, (3,4-epoxycyclohexyl)propyltributoxysilane, (3,4-epoxycyclohexyl)butyltrimethoxysilane, (3,4-epoxycyclohexyl) butyltriethoxysilane, (3,4-epoxycyclohexyl)butyltripropoxysilane, (3,4-
 15 epoxycyclohexyl)butyltributoxysilane, and so forth.

To help aid in its application, the interfacial coating may be initially provided in the form of a coating formulation that contains the hydrophobic resinous material (e.g., fluoropolymer) in combination with an organic solvent, which is typically a
 20 liquid at room temperature. When employed, such solvents typically constitute from about 90 wt.% to about 99.9 wt.%, in some embodiments from about 92 wt.% to about 99.8 wt.%, and in some embodiments, from about 95 wt.% to about 99.5 wt.% of the formulation, while the hydrophobic resinous material may constitute from about 0.1 wt.% to about 10 wt.%, in some embodiments from about 0.2 wt.% to about 8 wt.%, and in some embodiments, from about 0.5 wt.%
 25 to about 5 wt.% of the solution. The solvent(s) employed will depend in part on the nature of the resinous material, but generally include organic alcohols, hydrocarbon solvents, fluorinated hydrocarbon solvents, etc. For example, particularly suitable solvents for use with fluoropolymers include fluorinated hydrocarbon solvents, such as hydrofluoroethers, fluorinated ketones, fluorinated
 30 olefins, etc. In one particular embodiment, for instance, the coating formulation may contain a hydrofluoroether having the following general formula:



wherein:

x is 1 or 2;

one of R¹ and R² is a perfluoroaliphatic or perfluorocyclic group and the other is an aliphatic or a cyclic hydrocarbon group. For example, R¹ and/or R² may include substituted and nonsubstituted alkyl, aryl, and alkylaryl groups and their derivatives. Representative examples of suitable hydrofluoroethers include the following compounds: C₅F₁₁OC₂H₅, C₃F₇OCH₃, C₄F₉OCH₃, C₄F₉OC₂H₅, C₃F₇OCF(CF₃)CF₂OCH₃, C₄F₉OC₂F₄OC₂F₄OC₂H₅, C₄F₉O(CF₂)₃OCH₃, C₃F₇CF(OC₂H₅)CF(CF₃)₂, C₂F₅CF(OCH₃)CF(CF₃)₂, C₄F₉OC₂H₄OC₄F₉, etc. Particularly suitable are ethyl nonafluoroisobutyl ether and ethyl nonafluorobutyl ether, both of which are represented by the structure, C₄F₉OC₂H₅. Once applied, the coating may be dried, heated, and/or cured to remove any remaining solvent(s) and leave a coating of the resinous material at the desired location.

Prior to application of the interfacial coating, the anode lead may optionally be subjected to a cleaning process in which at least a portion, if not all, of any conductive material used to form the solid electrolyte is removed. This may occur along the entire length of the exposed wire, or it may occur only along a portion that is in direct proximity to the surface of the capacitor element. The removal of the conductive material may be accomplished using various techniques. In one embodiment, for example, the conductive material may be removed using a technique known as "laser wire cleaning." In such embodiments, the anode lead is placed in contact with a laser beam at those locations in which it is desired to remove the conductive material. In one embodiment, the laser is one in which the laser medium includes an aluminum and yttrium garnet (YAG) doped with neodymium (Nd) and the excited particles are neodymium ions Nd³⁺. Such lasers typically emit a light at a wavelength of about 1064 nanometers in the infrared spectrum. The laser may have any diameter suitable for the desired application. In some embodiments, the laser beam in the focused area has a diameter from about 0.05 mm to about 0.5 mm, in some embodiments from about 0.05 mm to about 0.3 mm, and in some embodiments from about 0.1 mm to about 0.15 mm. The laser may also include an optical head (e.g., lens), which as is well known in the art, primarily converges and focuses the laser beam to a focal point. The laser may also include a beam splitter.

III. Casing Material

As indicated, the capacitor element and anode lead are generally encapsulated with a casing material so that at least a portion of the anode and cathode terminations are exposed for mounting onto a circuit board. Referring again to Fig. 1, for instance, the capacitor element 33 and anode lead 16 may be encapsulated within a casing material 28 so that a portion of the anode termination 62 and a portion of the cathode termination 72 remain exposed.

The resinous matrix may be generally hydrophobic in nature. In certain embodiments, for example, the resinous matrix may contain a polycyanate containing at least two cyanate ester groups. When cured, for example, the polycyanate may form a polycyanurate having a triazine ring. Due to the high degree of symmetry in the triazine ring, where dipoles associated with the carbon-nitrogen and carbon-oxygen bonds are counterbalanced, the resulting polycyanurate can exhibit a relatively low degree of thermal expansion. Suitable polycyanates may include, for instance, bisphenol A dicyanate; the dicyanates of 4,4'-dihydroxydiphenyl, 4,4'-dihydroxydiphenyl oxide, resorcinyl, hydroquinone, 4,4'-thiodiphenol, 4,4'-sulfonyldiphenyl, 3,3',5,5'-tetrabromobisphenol A, 2,2',6,6'-tetrabromobisphenol A, 2,2'-dihydroxydiphenyl, 3,3'-dimethoxybisphenol A, 4,4'-dihydroxydiphenylcarbonate, dicyclopentadiene diphenol, 4,4'-dihydroxybenzophenone, 4,4'-dihydroxydiphenylmethane, tricyclopentadiene diphenol, etc.; the tricyanate of tris(hydroxyphenyl)methane, the tetracyanate of 2,2',4,4'-tetrahydroxydiphenyl methane, the polycyanate of a phenolformaldehyde condensation product (novolac); the polycyanate of a dicyclopentadiene and phenol condensation product; and so forth. If desired, the polycyanate may also contain one or more polycyclic aliphatic radicals containing two or more cyclic rings, such as a C₇-C₂₀ polycyclic aliphatic radical, including cyclopentadiene, norbornane, bornane, norbornadiene, trahydroindene, methyltrahydroindene, dicyclopentadiene, bicyclo-(2,2, 1)-hepta-2,5-diene, 5-methylene-2-norbornene, 5-ethylidene-2-norbornene, 5-propenyl-2-norbornene, 5-(4-cyclopentenyl)-2-norbornene, 5-cyclohexylidene-2-norbornene, 5-vinyl-2-norbornene, etc. In one particular embodiment, for instance, the polycyanate may be a dicyclopentadiene bisphenol cyanate ester. Without intending to be limited by theory, it is believed such polycyclic radicals can act as a nonpolar bridging group for the polycyanate,

which helps improve the resistance to thermal expansion.

The resinous matrix may also contain an epoxy resin, either alone or in combination with a polycyanate. When used in combination, the epoxy resin can react with the polycyanate to form a copolymer and/or crosslink with the

5 polycyanate resin when cured. Examples of suitable epoxy resins include, for instance, bisphenol A type epoxy resins, bisphenol F type epoxy resins, phenol novolac type epoxy resins, orthocresol novolac type epoxy resins, brominated epoxy resins and biphenyl type epoxy resins, cyclic aliphatic epoxy resins, glycidyl ester type epoxy resins, glycidylamine type epoxy resins, cresol novolac type

10 epoxy resins, naphthalene type epoxy resins, phenol aralkyl type epoxy resins, cyclopentadiene type epoxy resins, heterocyclic epoxy resins, etc. To help provide the desired degree of resistance to thermal expansion, however, it is particularly desirable to employ epoxy phenol novolac ("EPN") resins, which are glycidyl ethers of phenolic novolac resins. These resins can be prepared, for example, by

15 reaction of phenols with an excess of formaldehyde in the presence of an acidic catalyst to produce the phenolic novolac resin. Novolac epoxy resins are then prepared by reacting the phenolic novolac resin with epichlorohydrin in the presence of sodium hydroxide. Specific examples of the novolac-type epoxy resins include a phenol-novolac epoxy resin, cresol-novolac epoxy resin, naphthol-

20 novolac epoxy resin, naphthol-phenol co-condensation novolac epoxy resin, naphthol-cresol co-condensation novolac epoxy resin, brominated phenol-novolac epoxy resin, etc. Regardless of the type of resin selected, the resulting phenolic novolac epoxy resins typically have more than two oxirane groups and can be used to produce cured coating compositions with a high crosslinking density, which

25 can be particularly suitable for enhancing resistance to thermal expansion. One such phenolic novolac epoxy resin is poly[(phenyl glycidyl ether)-co-formaldehyde].

Other suitable resins are commercially available under the trade designation ARALDITE (e.g., GY289, EPN 1183, EP 1179, EPN 1139, and EPN 1138) from Huntsman.

30 The polycyanate and/or epoxy resin may be crosslinked with a co-reactant (hardener) to further improve the mechanical properties of the composition and also enhance its resistance to thermal expansion as noted above. Examples of such co-reactants may include, for instance, polyamides, amidoamines (e.g.,

aromatic amidoamines such as aminobenzamides, aminobenzanilides, and aminobenzenesulfonamides), aromatic diamines (e.g., diaminodiphenylmethane, diaminodiphenylsulfone, etc.), aminobenzoates (e.g., trimethylene glycol di-p-aminobenzoate and neopentyl glycol di-p-amino-benzoate), aliphatic amines (e.g., triethylenetetramine, isophoronediamine), cycloaliphatic amines (e.g., isophorone diamine), imidazole derivatives, guanidines (e.g., tetramethylguanidine), carboxylic acid anhydrides (e.g., methylhexahydrophthalic anhydride), carboxylic acid hydrazides (e.g., adipic acid hydrazide), phenolic-novolac resins (e.g., phenol novolac, cresol novolac, etc.), carboxylic acid amides, etc., as well as combinations thereof. Phenolic-novolac resins may be particularly suitable for use in the present invention.

The casing material may also contain an inorganic oxide filler. Such fillers are typically maintained at a high level of the casing material, such as from about 75 wt.% to about 99.5 wt.%, in some embodiments from about 76 wt.% to about 99 wt.%, and in some embodiments, from about 77 wt.% to about 90 wt.% of the casing material, while the resinous matrix typically constitutes from about 0.5 wt.% to about 25 wt.%, in some embodiments from about 1 wt.% to about 24 wt.%, and in some embodiments, from about 10 wt.% to about 23 wt.% of the casing material. The nature of the inorganic oxide fillers may vary, such as silica, alumina, zirconia, magnesium oxides, iron oxides (e.g., iron hydroxide oxide yellow), titanium oxides (e.g., titanium dioxide), zinc oxides (e.g., boron zinc hydroxide oxide), copper oxides, zeolites, silicates, clays (e.g., smectite clay), etc., as well as composites (e.g., alumina-coated silica particles) and mixtures thereof. Regardless of the particular fillers employed, however, a substantial portion, if not all, of the inorganic oxide fillers is typically in the form of vitreous silica, which is believed to further improve the moisture resistance of the casing material due to its high purity and relatively simple chemical form. Vitreous silica may, for instance, constitute about 30 wt.% or more, in some embodiments from about 35 wt.% to about 90 wt.%, and in some embodiments, from about 40 wt.% to about 80 wt.% of the total weight of fillers employed in the composition, as well as from about 20 wt.% to about 70 wt.%, in some embodiments from about 25 wt.% to about 65 wt.%, and in some embodiments, from about 30 wt.% to about 60 wt.% of the

entire composition. Of course, other forms of silica may also be employed in combination with the vitreous silica, such as quartz, fumed silica, cristabolite, etc.

Apart from the components noted above, it should be understood that still other additives may also be employed in the casing material, such as
5 photoinitiators, viscosity modifiers, suspension aiding agents, pigments, stress reducing agents, coupling agents (e.g., silane coupling agents), stabilizers, etc. When employed, such additives typically constitute from about 0.1 to about 20 wt.% of the total composition.

The particular manner in which the casing material is applied to the
10 capacitor element may vary as desired. In one particular embodiment, the capacitor element is placed in a mold and the casing material is applied to the capacitor element so that it occupies the spaces defined by the mold and leaves exposed at least a portion of the anode and cathode terminations. The casing material may be initially provided in the form of a single or multiple compositions.
15 For instance, a first composition may contain the resinous matrix and filler and the second composition may contain a co-reactant. Regardless, once it is applied, the casing material may be heated or allowed to stand at ambient temperatures so that the resinous matrix is allowed to crosslink with the co-reactant, which thereby causes the casing material to cure and harden into the
20 desired shape of the case. For instance, the casing material may be heated to a temperature of from about 15°C to about 150°C, in some embodiments from about 20°C to about 120°C, and in some embodiments, from about 25°C to about 100°C.

Although by no means required, a moisture barrier layer may also be
25 employed that coats all or a portion of the casing material. The moisture barrier layer is generally formed from a hydrophobic material such as described above, e.g., silicone, fluoropolymer, organometallic compound, etc.

The present invention may be better understood by reference to the following examples.

30

Test Procedures

Capacitance

The capacitance may be measured using a Keithley 3330 Precision LCZ meter with Kelvin Leads with 2.2 volt DC bias and a 0.5 volt peak to peak

sinusoidal signal. The operating frequency may be 120 Hz and the temperature may be $23^{\circ}\text{C} \pm 2^{\circ}\text{C}$. In some cases, the “wet-to-dry” capacitance can be determined. The “dry capacitance” refers to the capacitance of the part before application of the solid electrolyte, graphite, and silver layers, while the “wet

5 capacitance” refers to the capacitance of the part after formation of the dielectric, measured in 14% nitric acid in reference to 1 mF tantalum cathode with 10 volt DC bias and a 0.5 volt peak to peak sinusoidal signal after 30 seconds of electrolyte soaking.

Equivalent Series Resistance (ESR)

10 Equivalence series resistance may be measured using a Keithley 3330 Precision LCZ meter with Kelvin Leads 2.2 volt DC bias and a 0.5 volt peak to peak sinusoidal signal. The operating frequency may 100 kHz and the temperature may be $23^{\circ}\text{C} \pm 2^{\circ}\text{C}$.

Dissipation Factor

15 The dissipation factor may be measured using a Keithley 3330 Precision LCZ meter with Kelvin Leads with 2.2 volt DC bias and a 0.5 volt peak to peak sinusoidal signal. The operating frequency may be 120 Hz and the temperature may be $23^{\circ}\text{C} \pm 2^{\circ}\text{C}$.

Leakage Current

20 Leakage current may be measured using a leakage test meter at a temperature of $23^{\circ}\text{C} \pm 2^{\circ}\text{C}$ and at the rated voltage after a minimum of 60 seconds.

Humidity Testing

Humidity testing is based on standard IEC 68-2-67:1995, severity III (85°C ,

25 85% relative humidity). The test sample size is 25 parts and the tested parts are loaded with rated voltage at test conditions. Leakage current is measured at 0, 120, 250, 500 and 1,000 hours at recovered samples. The recovery time after the test conditions may be from 2 to 24 hours. After each measurement, the ratio of short circuit failures from all tested parts is calculated. Leakage limit for short

30 circuit (μA) is set as a multiple of nominal capacitance (μF) and nominal voltage (V) of the tested parts.

EXAMPLE 1

70,000 $\mu\text{FV/g}$ tantalum powder was used to form anode samples. Each

anode sample was embedded with a tantalum wire, sintered at 1270°C, and pressed to a density of 5.8 g/cm³. The resulting pellets had a size of 4.9 x 3.45 x 1.2 mm. The pellets were anodized to 20.0 volts in water/phosphoric acid electrolyte with a conductivity of 8.6 mS/cm at a temperature of 85°C to form the dielectric layer. The pellets were anodized again to 80 volts in a water/boric acid/disodium tetraborate with a conductivity of 2.0 mS/cm at a temperature of 30°C for 25 seconds to form a thicker oxide layer built up on the outside.

A conductive polymer coating was then formed by dipping the anode into a butanol solution of iron (III) toluenesulfonate (Clevios™ C, H.C. Starck) for 5 minutes and consequently into 3,4-ethylenedioxythiophene (Clevios™ M, H.C. Starck) for 1 minute. After 45 minutes of polymerization, a thin layer of poly(3,4-ethylenedioxythiophene) was formed on the surface of the dielectric. The anode was washed in methanol to remove reaction by-products, anodized in a liquid electrolyte, and washed again in methanol. This process was repeated 6 times. Thereafter, the parts were dipped into a dispersed poly(3,4-ethylenedioxythiophene) having a solids content of 2.0% and viscosity 20 mPa.s (Clevios™ K, Heraeus). Upon coating, the parts were dried at 125°C for 20 minutes. This process was repeated 3 times. Thereafter, the parts were dipped into a dispersed poly(3,4-ethylenedioxythiophene) having a solids content of 2.0% and viscosity 160 mPa.s (Clevios™ K, Heraeus). Upon coating, the parts were dried at 125°C for 20 minutes. This process was repeated 12 times. The parts were then dipped into a graphite dispersion and dried. Finally, the parts were dipped into a silver dispersion and dried.

Multiple parts (2,000) of 330μF/6.3V capacitors with an “L₁” distance of approximately 0.90 mm were made in this manner and encapsulated in a silica resin. The length (“L₂”) of the resulting capacitor was approximately 7.5 mm such that the ratio of L₁/L₂ was approximately 0.12.

EXAMPLE 2

Capacitors were formed in the manner described in Example 1, except that the resulting pellets had a size of 4.7 x 3.45 x 1.25 mm. Finally, the parts were encapsulated in a silica resin. Multiple parts (6,000) of 330μF/6.3V capacitors with an “L₁” distance of approximately 1.1 mm were formed. The length (“L₂”) of the resulting capacitor was approximately 7.5 mm such that the ratio of L₁/L₂ was

approximately 0.15.

EXAMPLE 3

Capacitors were formed in the manner described in Example 1, except that the resulting pellets had a size of 4.15 x 3.45 x 1.5 mm. Finally, the parts were
 5 encapsulated in a silica resin. Multiple parts (3,000) of 330 μ F/6.3V capacitors with an “L₁” distance of approximately 1.45 mm were formed. The length (“L₂”) of the resulting capacitor was approximately 7.5 mm such that the ratio of L₁/L₂ was approximately 0.19.

10 Twenty five (25) parts were subjected to humidity testing as described above. The results are set forth below.

		EXAMPLE 1	EXAMPLE 2	EXAMPLE 3
L ₁ (mm)		1.45	1.1	0.9
L ₂ (mm)		7.5	7.5	7.5
L ₁ /L ₂		0.19	0.15	0.12
Humidity test		% of Short Circuits		
Test time (hrs)	0	0	0	0
	120	0	-	4
	250	-	0	-
	500	0	0	52
	1,000	0	0	60

These and other modifications and variations of the present invention may be practiced by those of ordinary skill in the art, without departing from the spirit and scope of the present invention. In addition, it should be understood that
 15 aspects of the various embodiments may be interchanged both in whole or in part. Furthermore, those of ordinary skill in the art will appreciate that the foregoing description is by way of example only, and is not intended to limit the invention so further described in such appended claims.

WHAT IS CLAIMED IS:

1. A solid electrolytic capacitor having a length in a longitudinal direction, comprising:
 - a capacitor element having opposing front and rear surfaces, opposing upper and lower surfaces, and opposing side surfaces, wherein the capacitor element contains a sintered porous anode body, a dielectric that overlies the anode body, and a solid electrolyte that overlies the dielectric;
 - an anode lead extending from the front surface of the capacitor element in the longitudinal direction;
 - an anode termination that is in contact with the anode lead at a connection region, wherein a distance is defined between the connection region and the front surface of the capacitor element, and further wherein the ratio of the distance between the connection region and the front surface of the capacitor element to the length of the capacitor is about 0.13 or more;
 - a cathode termination that is in electrical connection with the solid electrolyte;
 - a casing material that encapsulates the capacitor element and anode lead and leaves exposed at least a portion of the anode termination and cathode termination for external contact; and
 - an interfacial coating that is disposed on at least a portion of the anode termination and/or cathode termination and is in contact with the casing material.
2. The solid electrolytic capacitor of claim 1, wherein the ratio of the distance between the connection region and front surface of the capacitor element to the length of the capacitor is about 0.15 or more.
3. The solid electrolytic capacitor of claim 1, wherein the distance between the connection region to the front surface of the capacitor element is from about 1 to about 2 millimeters.
4. The solid electrolytic capacitor of claim 1, wherein the length of the capacitor is from about 2 to about 15 millimeters.
5. The solid electrolytic capacitor of claim 1, wherein the interfacial coating covers at least a portion of the anode termination.
6. The solid electrolytic capacitor of claim 5, wherein the interfacial coating also covers at least a portion of the anode lead.

7. The solid electrolytic capacitor of claim 5, wherein the interfacial coating includes a fluoropolymer, silicone polymer, organometallic compound, or a combination thereof.

8. The solid electrolytic capacitor of claim 1, wherein the resinous matrix contains a polycyanate containing at least two cyanate ester groups.

9. The solid electrolytic capacitor of claim 1, wherein the resinous matrix contains an epoxy resin.

10. The solid electrolytic capacitor of claim 1, wherein the resinous matrix further includes an inorganic oxide filler in an amount from about 75 wt.% to about 99.5 wt.% of the matrix.

11. The solid electrolytic capacitor of claim 10, wherein the inorganic oxide filler includes silica.

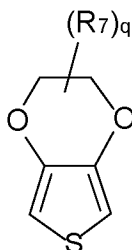
12. The solid electrolytic capacitor of claim 1, wherein the capacitor element further comprises a cathode coating that contains a metal particle layer that overlies the solid electrolyte, wherein the metal particle layer includes a plurality of conductive metal particles.

13. The solid electrolytic capacitor of claim 12, wherein the metal particles include silver.

14. The solid electrolytic capacitor of claim 1, wherein the anode body includes tantalum.

15. The solid electrolytic capacitor of claim 1, wherein the solid electrolyte includes a conductive polymer.

16. The solid electrolytic capacitor of claim 15, wherein the conductive polymer has repeating units of the following formula:



wherein,

R_7 is a linear or branched, C_1 to C_{18} alkyl radical, C_5 to C_{12} cycloalkyl radical, C_6 to C_{14} aryl radical, C_7 to C_{18} aralkyl radical, or a combination thereof; and

q is an integer from 0 to 8.

17. The solid electrolytic capacitor of claim 16, wherein the conductive polymer is poly(3,4-ethylenedioxythiophene) or a derivative thereof.

18. The solid electrolytic capacitor of claim 15, wherein the solid electrolyte also contains a polymeric counterion.

19. The solid electrolytic capacitor of claim 1, further comprising an external polymer coating that overlies the solid electrolyte and contains pre-polymerized conductive polymer particles and a cross-linking agent.

AMENDED CLAIMS**received by the International Bureau on 22 October 2019 (22.10.2019)**

1. A solid electrolytic capacitor having a length in a longitudinal direction, comprising:

a capacitor element having opposing front and rear surfaces, opposing upper and lower surfaces, and opposing side surfaces, wherein the capacitor element contains a sintered porous anode body, a dielectric that overlies the anode body, and a solid electrolyte that overlies the dielectric;

an anode lead extending from the front surface of the capacitor element in the longitudinal direction;

an anode termination that is in contact with the anode lead at a connection region, wherein a distance is defined between the connection region and the front surface of the capacitor element, and further wherein the ratio of the distance between the connection region and the front surface of the capacitor element to the length of the capacitor is about 0.13 or more;

a cathode termination that is in electrical connection with the solid electrolyte;

a casing material that encapsulates the capacitor element and anode lead and leaves exposed at least a portion of the anode termination and cathode termination for external contact; and

an interfacial coating that is disposed on at least a portion of the anode termination and/or cathode termination and is in contact with the casing material.

2. The solid electrolytic capacitor of claim 1, wherein the ratio of the distance between the connection region and front surface of the capacitor element to the length of the capacitor is about 0.15 or more.

3. The solid electrolytic capacitor of claim 1, wherein the distance between the connection region to the front surface of the capacitor element is from about 1 to about 2 millimeters.

4. The solid electrolytic capacitor of claim 1, wherein the length of the capacitor is from about 2 to about 15 millimeters.

5. The solid electrolytic capacitor of claim 1, wherein the interfacial coating covers at least a portion of the anode termination.

6. The solid electrolytic capacitor of claim 5, wherein the interfacial coating

also covers at least a portion of the anode lead.

7. The solid electrolytic capacitor of claim 5, wherein the interfacial coating includes a fluoropolymer, silicone polymer, organometallic compound, or a combination thereof.

8. The solid electrolytic capacitor of claim 1, wherein the casing material contains a polycyanate containing at least two cyanate ester groups.

9. The solid electrolytic capacitor of claim 1, wherein the casing material contains an epoxy resin.

10. The solid electrolytic capacitor of claim 1, wherein the casing material further includes an inorganic oxide filler in an amount from about 75 wt.% to about 99.5 wt.% of the matrix.

11. The solid electrolytic capacitor of claim 10, wherein the inorganic oxide filler includes silica.

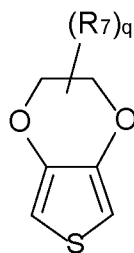
12. The solid electrolytic capacitor of claim 1, wherein the capacitor element further comprises a cathode coating that contains a metal particle layer that overlies the solid electrolyte, wherein the metal particle layer includes a plurality of conductive metal particles.

13. The solid electrolytic capacitor of claim 12, wherein the metal particles include silver.

14. The solid electrolytic capacitor of claim 1, wherein the anode body includes tantalum.

15. The solid electrolytic capacitor of claim 1, wherein the solid electrolyte includes a conductive polymer.

16. The solid electrolytic capacitor of claim 15, wherein the conductive polymer has repeating units of the following formula:



wherein,

R_7 is a linear or branched, C_1 to C_{18} alkyl radical, C_5 to C_{12} cycloalkyl

radical, C₆ to C₁₄ aryl radical, C₇ to C₁₈ aralkyl radical, or a combination thereof;
and

q is an integer from 0 to 8.

17. The solid electrolytic capacitor of claim 16, wherein the conductive polymer is poly(3,4-ethylenedioxythiophene) or a derivative thereof.

18. The solid electrolytic capacitor of claim 15, wherein the solid electrolyte also contains a polymeric counterion.

19. The solid electrolytic capacitor of claim 1, further comprising an external polymer coating that overlies the solid electrolyte and contains pre-polymerized conductive polymer particles and a cross-linking agent.

A. CLASSIFICATION OF SUBJECT MATTER**H01G 9/15(2006.01)i, H01G 11/44(2013.01)i, H01G 11/48(2013.01)i, H01G 9/00(2006.01)i**

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

H01G 9/15; H01G 9/00; H01G 9/025; H01G 9/07; H01G 9/08; H02G 3/08; H01G 11/44; H01G 11/48

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

Korean utility models and applications for utility models

Japanese utility models and applications for utility models

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

eKOMPASS(KIPO internal) & Keywords: solid electrolytic capacitor, solid electrolyte, connection region, anode, cathode

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2010-0246100 A1 (TAKASHI UMEMOTO et al.) 30 September 2010 See paragraphs [0038]-[0114] and figures 1-3.	1-19
Y	US 2004-0104038 A1 (SHINJI NAKAMURA et al.) 03 June 2004 See paragraphs [0122]-[0123] and figure 20.	1-19
Y	US 2017-0207032 A1 (AVX CORPORATION) 20 July 2017 See paragraphs [0043]-[0044] and claims 1, 8, 14.	16-19
A	US 2011-0096466 A1 (IVAN HORACEK et al.) 28 April 2011 See paragraphs [0010]-[0051] and figure 1.	1-19
A	US 2006-0187617 A1 (SADAMU TOIDA et al.) 24 August 2006 See paragraphs [0031]-[0032] and figures 3A-3B.	1-19

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

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

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

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

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

"&" document member of the same patent family

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INTERNATIONAL SEARCH REPORT

Information on patent family members

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