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Characteristics of aluminium solid electrolytic capacitors using a conducting polymer

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Abstract

In order to form an electrochemically polymerized polypyrrole film on an electrically insulated dielectric layer surface, a conductive precoating layer was first deposited, at the expense of electrical conductivity. Using the precoating layer as the anode, a polypyrrole layer was then deposited electrochemically in preparation for the fabrication of a solid electrolytic capacitor in which the composite conducting polymer layer was used as a solid electrolyte. Soluble polyaniline could be used as a conductive precoating layer as well as polypyrrole formed by chemical oxidizing polymerization. The capacitor using the composite solid electrolyte presented excellent impedance frequency and temperature characteristics; moreover, the solid electrolyte showed 'self-healing' and non-polar behaviour.

Keywords: Aluminium electrolytic capacitors; Solid electrolyte; Conducting polymers; Polypyrrole; Polyaniline

1. Introduction

In recent years high performance characteristics, including low impedance at high frequencies, thermal stability in molten solder to enable its use in surface mounting technology and improved reliability, have become of great importance for electrolytic capacitors.

Conventional aluminium electrolytic capacitors present many disadvantages such as high impedance and thermal instability, in addition to the problem of liquid electrolyte leakage, owing to the use of a low-conductive (10^{-2}–10^{-3} S/cm) and thermally unstable ionic liquid electrolyte. While tantalum electrolytic capacitors achieve improved thermal stability by employing pyrolytic manganese dioxide, the impedance frequency characteristics are not improved because of the low conductivity of manganese dioxide, in the range from 10^{-2} to 10^{-1} S/cm.

To cope with this situation, a solid aluminium electrolytic capacitor using an organic semiconductor, TCNQ (7,7,8,8-tetracyanoquinodimethane) complex salt was developed in 1983 [1]. Specific TCNQ complex salts have high conductivity even after melting and solidification by cooling within a certain period of time. Thus TCNQ complex salts can be impregnated into etched aluminium foil by melting and cooling to form a solid electrolyte. This capacitor presents excellent low-impedance frequency characteristics and does not suffer deterioration due to drying up of the electrolyte.

In our previous report [2], more than two hundred TCNQ complex salts were synthesized in an attempt to discover salts with a high-melting point; of these, the salt with the highest melting point which was available for use in a melting method was N-β-phenethyl-3,5-lutidinium(TCNQ)$_2$; its melting point was 257 °C. Therefore, a capacitor prepared using this salt would not be able to tolerate a soldering temperature of 260 °C.

We have developed solid aluminium and tantalum electrolytic capacitors using composite polypyrrole as solid electrolytes, which have high conductivity and thermal stability at the soldering temperature [3,4]. The solid electrolyte was composed of a polypyrrole precoating layer formed by a chemical oxidizing polymerization and an electrochemically polymerized polypyrrole [5,6].

In this paper we report on the comparison of the performance of conductive precoating layers and the specific characteristics of the capacitors.

2. Experimental

Etched aluminium foil with lead wire, serving as the anode lead of a capacitor, was electrically oxidized at 50 V to form an aluminium oxide dielectric layer. The surface was then covered with a conductive precoating layer, such as a chemically oxidizing polymer, and was subjected to reforming at

40 V. This aluminium foil was immersed in an electrolyte solution containing 0.2 mol/l of pyrrole monomer and 0.1 mol/l of supporting electrolyte. An auxiliary electrode was touched with the precoating layer and using this layer as the anode, galvanostatic polymerization was carried out. After the aluminium foil was coated with colloidal carbon and silver paste, a cathode lead wire was attached, and the surface was then covered with epoxy resin. Further details of the preparation process are described previously in Ref. [5].

Capacitance (C), dielectric loss (tan δ) were measured at 120 Hz and the equivalent series resistance (ESR) was measured at 100 kHz by an impedance analyzer (Hewlett-Packard, Model 4194A).

Soluble polyaniline was synthesized by the MacDirmid method [7]. A 1% solution of the emeraldine base polyaniline in N-methyl-2-pyrrolidinone (NMP) with 0.5% solution of citric acid was then prepared. After the etched aluminium foil was immersed in this solution, it was dried at 100 °C to form a conductive precoating layer. Successive procedures were carried out under the same experimental conditions as described above.

3. Results and discussion

3.1. Comparison of conductive precoationg layer performance

To prevent the aluminium oxide dielectric layer deteriorating with moisture, it is important to use a polypyrrole film prepared by electrochemical polymerization; such a film has not only high conductivity and considerable stability, but offers also good mechanical strength.

In our previous paper [8], polypyrrole was electrochemically polymerized with a variety of anions, in which aromatic sulfonate anions such as paratoluene sulfonate, benzene disulfonate and β-naphthalene sulfonate enhanced both the thermal stability of the polypyrrole film at 145 °C and the thermal reliability of an aluminium electrolytic capacitor at 125 °C. The capacitance change and tan δ showed almost no change over a 5000 h endurance test; after 100 h of a moisture endurance test, in which the capacitor was exposed to a 121 °C/2 atm steam environment, the capacitance and tan δ increased by 5 and 200%, respectively.

The solid electrolyte was composed of a polypyrrole layer formed by chemically oxidizing polymerization (CP–PPy) and an electrochemically polymerized polypyrrole (EP–PPy).

For comparison, soluble polyaniline (S-PAn) was formed as the conductive precoating layer. In general, mixing soluble polyaniline with acid causes doping to form insoluble conductive polyaniline. However, when mixing with specific carboxylic acids, such as citric acid, phthalic acid, fumaric acid and maleic acid (pKa is over 2.2), doping did not occur at room temperature. Doping of soluble polyaniline with citric acid (pKa of 2.87) was effected by heating to temperatures

over 100 °C, at which the conductivity was as low as 2.4×10^{-4} S/cm; however, the dopant is expected to oxidize anodically the aluminium.

The order of thermal stability of polyaniline with carboxylic acids is as follows: citric acid > phthalic acid > maleic acid > fumaric acid.

Figs. 1 and 2 show the initial characteristics and the time dependences of the capacitor characteristics of the thermal and moisture endurance test, respectively. The capacitance change was around 2% and tan δ showed almost no change after a 1000 h endurance test at 125 °C. After the capacitor was exposed to an 85 °C and 85% RH atmosphere for 1000 h, the capacitance and tan δ increased by 7 and 200%, respectively. The foregoing results show that soluble polyaniline can be used as a precoating compound in stead of CP–PPy.

It was feared that the proton added to the polyaniline N atom would damage the thin dielectric layer in the endurance tests, because the dielectric layer is thin (about 0.1 μm); moreover, reversal doping occurs readily in moisture endur-
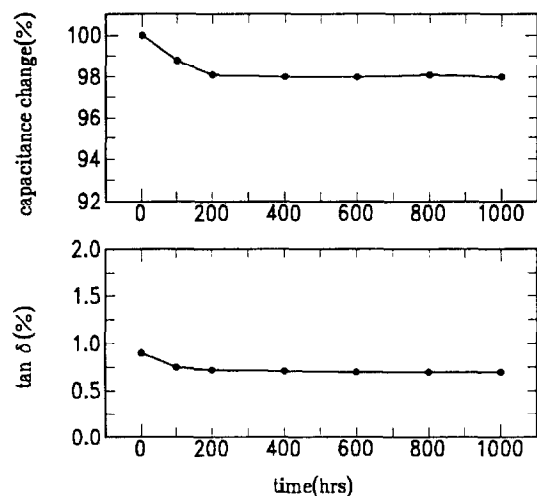

Fig. 1. Electrical characteristics vs. time at 125 °C for aluminium solid electrolytic capacitor with polyaniline precoating.
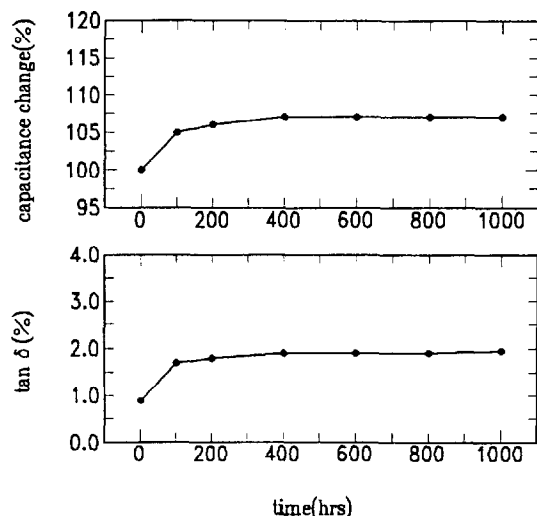

Fig. 2. Electrical characteristics vs. time at 85 °C and 85% RH atmosphere for aluminium solid electrolytic capacitor with polyaniline precoating.

ance tests. However, it is clear that there are no problems when using soluble polyaniline as a precoating, and the composite solid electrolyte consisting of S-PAn/EP–PPy has the same characteristics as those of CP–PPy/EP–PPy.

3.2. Capacitor characteristics

Fig. 3 shows a photograph of the trial products, which are thin, square-shaped chip-type capacitors. They have a width of 4.3 mm, length 7.3 mm and height 2.0 mm, and a nominal capacitance of 10 μF at a working voltage of 6.3 V.

As described in Ref. [5], this capacitor has a low impedance in the high-frequency region from several hundred kHz up to MHz frequencies, comparable with the impedance of film capacitors and ceramic capacitors. Fig. 4 shows impedance frequency characteristics.

Fig. 5 shows temperature versus conductivity of the composite electrolyte, where the measured conductivity was 21.3 S/cm at 20 °C. The excellent impedance frequency
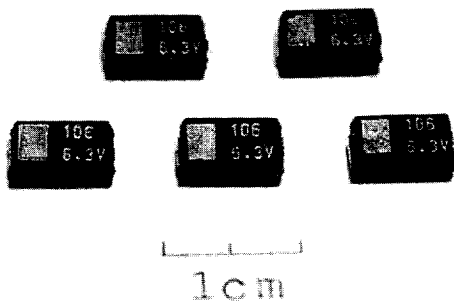
characteristics must be due to this high conductivity of the electrolyte.

Fig. 6 shows temperature versus capacitance and dielectric loss. In the case of liquid electrolytes, the dependences are marked especially at low temperatures, because the ionic conductivity is low at low temperatures; on the other hand, the values for composite electrolytes are changed by only 3% at −40 °C and 4% at 125 °C. The foregoing result indicates that the conductivity of the composite electrolyte is almost temperature independent. The activation energy of the composite electrolyte was 1.48×10^{-2} eV.

3.3. Leakage current characteristics

Since the dielectric of an electrolytic capacitor is formed by anodic oxidation of valve metals, a dielectric layer consisting of aluminium oxide or tantalum oxide has a rectifying
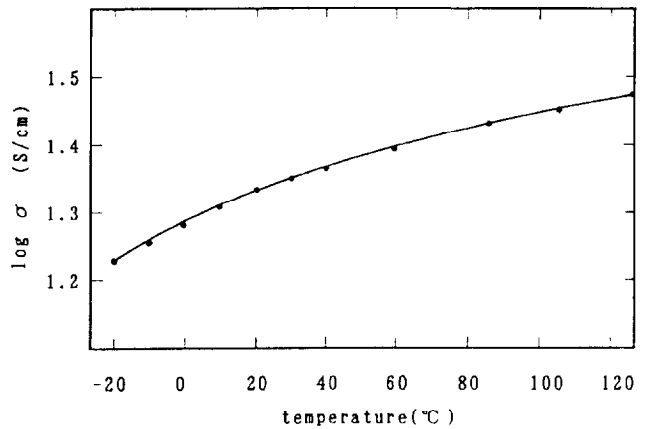

Fig. 3. Photograph of the trial products.

Fig. 4. Frequency characteristics of impedance for various capacitors.

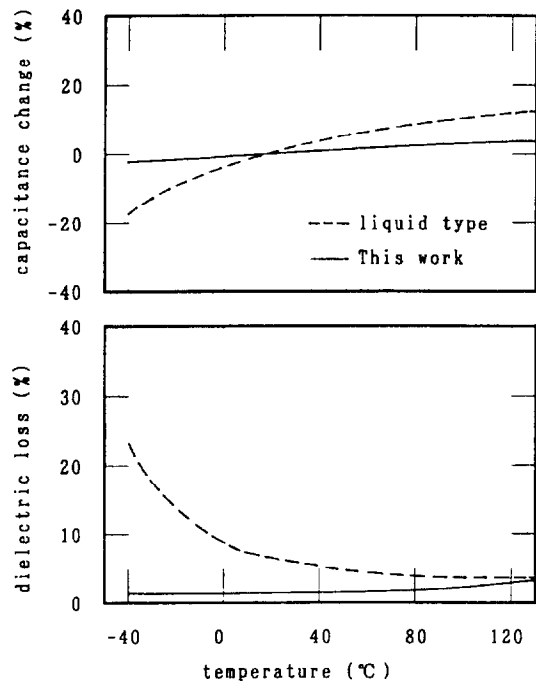Fig. 5. Temperature vs. conductivity of composite solid electrolyte.

Fig. 6. Temperature vs. capacitance change and dielectric loss of aluminium electrolytic capacitor at 120 Hz (capacitance: 3.3 μF).

action. Therefore, an electrolytic capacitor shows a polarity; in particular, a tantalum electrolytic capacitor breaks down readily under a slight negative voltage. This is the greatest drawback of electrolytic capacitors.

To study the leakage current characteristics, the leakage current (I) of 16 working voltage capacitors was measured when charged with positive and negative potentials (V). Fig. 7 shows the V–I curve of several kinds of capacitor for comparison: an aluminium electrolytic capacitor formed using polypyrrole (PA), an aluminium electrolytic capacitor formed using TCNQ complex salt (OS), a conventional liquid aluminium electrolytic capacitor (CE) and a conventional tantalum electrolytic capacitor formed using manganese dioxide (CS).

The leakage current of CS increases drastically to 8.4 μA at − 2 V to result in a short circuit. The CE is shorted at − 10 V, and OS, which has relatively high endurance under a reversed potential, broke down to pass 30 μA at − 16 V. On the other hand, the leakage current of PA is only 2.9 μA at − 16 V; moreover, though the charged potential is quickly reversed from − 16 to 16 V , the leakage current is only 0.03 μA.

In general, the forming voltage of a solid electrolytic capacitor is set such that the ratio of forming voltage (FV) to working voltage (WV), FV/WV, is between 3 and 5. The PA was formed at 50 V, therefore the ratio FV/WV is 3.1. It is seen that the leakage current characteristics of PA under a reversed potential is superior to that of the other capacitors.

These results suggest that deoxidizing reactions of the dielectric metal oxide layer occur easily in the CS-, CE- and OS-types, but do not occur easily in the PA electrolyte, because the polypyrrole does not take part in the redox reaction in a charged state.

3.4. Self-healing behaviour of polypyrrole electrolytes

In addition to an electrolyte acting as a true cathode in a solid electrolytic capacitor, there should be the ability to restore defects in the dielectric, i.e. self-healing capabilities. Since a conventional liquid-type aluminium capacitor uses salts of carboxylic acids as the electrolyte, defects can be restored by anodic oxidation of aluminium under potential. The self-healing was studied in the case of TCNQ complex salts [9], in which the current efficiency of the anodic oxidation of aluminium by TCNQ complex salts was higher than that of MnO_2.

We observed the self-healing behaviour in the composite solid electrolyte as well. Fig. 8 shows the leakage current as a function of time in which a composite solid-type aluminium capacitor with a working voltage of 16 V is charged to 20 V. Although during the initial charging the current increases rapidly due to the dielectric absorption, it decreases slowly with vibrations as the time proceeds. Though the current is 0.1 μA at 100 s, during this period of time the dielectric absorption is expected to be relieved, it decreases to 0.007 μA after 1800 s.

Fig. 9 shows the results when the capacitor is charged in two steps: 10 V in the first step, followed by 20 V after 600 s. The current decreases from 0.015 μA at 100 s to 0.003 μA 600 s later. Then after charging to 20 V for 1200 s it decreases to 0.006 μA, resulting in the same current value as for a one-step charging.

When the voltage is charged under 100 °C, the current decreases by two orders of magnitude from the initial current after 30 min.

These results indicate that two important factors in the 'self-healing' are the potential and the temperature. The self-healing behaviour is also observed when the reversed potential is turned on.

It is assumed that the self-healing is caused by either an insulating reaction of the solid electrolyte occurring at the contact surface between the aluminium and the solid electro-
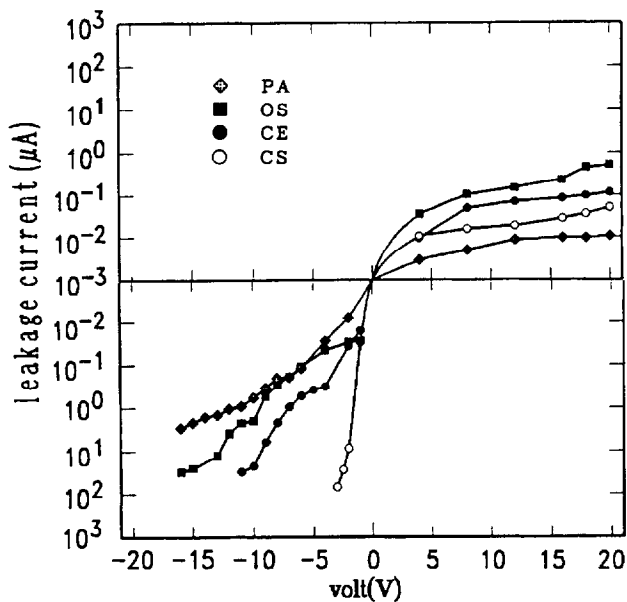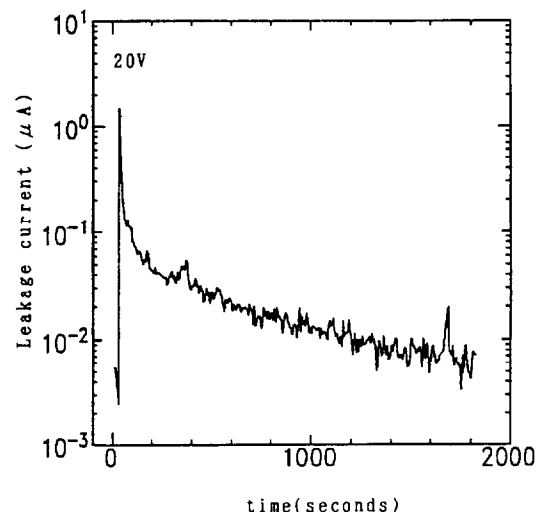

Fig. 7. Voltage vs. leakage current of several kinds of capacitor. PA: polypyrrole conducting polymer aluminium capacitor; OS: TCNQ complex salt aluminium capacitor; CE: conventional liquid aluminium capacitor, and CS: manganese dioxide tantalum capacitor.

Fig. 8. Leakage current vs. time (one-step charging).
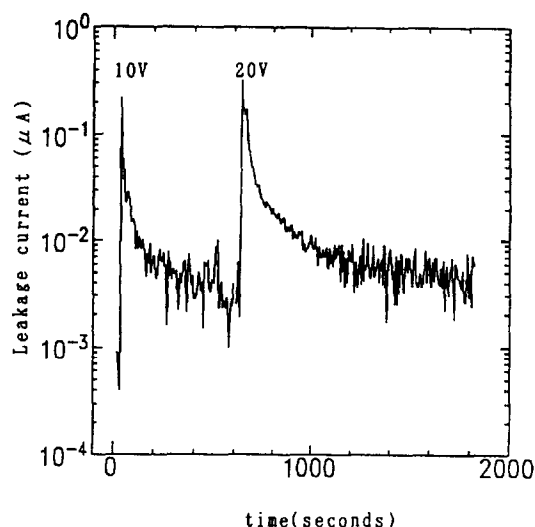
time(seconds)

Fig. 9. Leakage current vs. time (two-step charging).

lyte due to local heating and resulting undoping of poly-pyrrole when the anodic potential is applied or an anodic oxidation of aluminium is in contact with the solid electrolyte, probably a very small amount of water that might be present in the solid electrolyte could contribute to the oxidation.

4. Conclusions

We have developed a new type of an aluminium electro-lytic capacitor in which a solid electrolyte is combined with a precoating layer consisting of a slightly higher resistance conducting polymer and an electrolytically polymerized polypyrrole.

Soluble polyaniline shows good performance as a pre-coating layer, as does polypyrrole formed by chemical oxi-dizing polymerization.

Capacitors using composite conducting polymers show excellent frequency and temperature characteristics; more-over, the solid electrolyte exhibits 'self-healing' behaviour and good leakage current characteristics like a non-polar. Further work on this subject is now in progress.

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