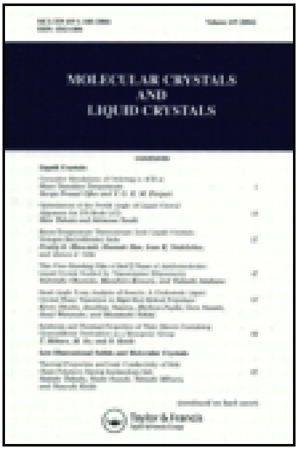

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Electrolytic Capacitor Employing Polypyrrole as Solid Electrolyte

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ELECTROLYTIC CAPACITOR EMPLOYING POLYPYRROLE AS SOLID ELECTROLYTE

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Abstract New type of aluminum and tantalum electrolytic capacitors employing polypyrrole as solid electrolytes were developed. The surface of a dielectric is covered with electroconductive pre-coating thin layer of polypyrrole prepared by chemical oxidative polymerization. Then utilizing this layer as an anode, electrochemically polymerized polypyrrole is filled in micropores.

INTRODUCTION

Most of commercial available aluminum electrolytic capacitors have some disadvantages, such as high impedance at high frequency regions and poor thermal stability, because they employ ionic liquid electrolytes as true cathodes. In tantalum electrolytic capacitors thermal stability is improved because of employing manganese dioxide solid electrolyte formed by pyrolysis. However the impedance characteristics are not still improved because the conductivity is low as the range from 10^{-2} to 10^{-1} S/cm [1].

Electroconductive polypyrrole has been attractived as solid electrolyte because it has high conductivity of the range from 10 to 10^{2} S/cm [2] and moderate environmental stability [3]. There are two methods to polymerize polypyrrole. One is chemical oxidative method [4] and the other is electrochemical method [2]. The electrochemically polymerized polypyrrole shows high conductivity and good physical strengths, therefore it is suitable to the solid electrolyte. However it is impossible to polymerize polypyrrole electrochemically because the surface of electrolytic capacitor is covered with a insulated dielectric layer.

We have developed aluminum and tantalum solid capacitors employing only polypyrrole polymer prepared by combination of chemical oxidative polymerization and electrochemical polymerization [5,6] as electrolytes.

EXPERIMENTAL

Preparation of aluminum electrolytic capacitor; A 2.2mm × 10mm etched aluminum foil with aluminum wire lead was anodized at 49V to form dielectric layer. Then this was immersed in 6M of pyrrole/ethanol soln., continuously in 0.1M of ammonium persulfate aqueous soln. to prepare chemical oxidative polymerized polypyrrole. This aluminum foil was immersed in CH_3CN containing 0.2 M of pyrrole and 0.1M of supporting electrolyte. An auxiliary electrode was touched with the surface of the chemical oxidative polymerized polypyrrole, and using this as an anode a galvanostatic electrochemical polymerization was carried out. After then the aluminum foil was coated with colloidal carbon and silver paint, and was molded with epoxy resin after a cathode lead was taken out. Capacitance, $\tan\delta$ (dissipation factor) ,ESR(Equivalent Series Resistance) and impedance were measured as a function of frequency, temperature and time.

Preparation of tantalum electrolytic capacitor; A tantalum porus sintered slug, of which the product of capacitance(μF) and forming voltage(V) per g-unit is about 10,000, was anodized at 100V to form a dielectric layer. Then the slug was immersed in 20 wt% of hydrogen peroxide soln. containing 3wt% of sulfuric acid, continuously in pyrrole monomer to prepare chemical oxidative polymerized polypyrrole. An electrochemical polymerization and succeeding procedures were carried out as same as the experiment of the aluminum electrolytic capacitor.

COMPARISION OF CONDUCTIVE PRE-COATING LAYERS

The comparition of conductive pre-coating layers was examined on tantalum electrolytic capacitor. At first we examined the difference between polypyrrole prepared by a chemical oxidative polymerization (CP) and that by an electrochemical polymerization (EP).

Table I shows initial electrical characteristics of two types of capacitors. One has polypyrrole solid electrolyte prepared by only 10 times of CP and the other prepared by a combination of 2 times of CP and 20 minutes of EP(0.5mA/unit). The former shows high ESR value and tanδ because the polypyrrole prepared by CP is porosity and the conductivity is estimated in the region of 1~10 S/cm from preliminary experiments. The latter shows improved characteristics because EP gives high conductivity and high density polypyrrole.

TABLEL I Initial Characteristics of Tantalum Capacitor.

Polypyrrole	Capacitance/C_{liq} (%)	tanδ (%)	ESR (mΩ)
CP	88.1	5.78	2710
CP and EP	96.0	0.80	185

C_{liq} :Capacitance measured in liquid electrolyte

Then the comparision of manganese dioxide and polypyrrole prepared by CP as a conductive pre-coating layer was examined. Preparation methods of solid electrolyte are as follows: A;10 times of pyrolysis preparation of MnO_2. B;10 times of pyrolysis preparation of MnO_2 and electrochemical polymerization of polypyrrole. C;5times of pyrolysis preparation of MnO_2 and electrochemical polymerization of polypyrrole. D;2 times of chemical oxidative polymerization and electrochemical polymerization of polypyrrle. Fig.1 shows frequency characteristics of impedance of these capacitors. The order of impedance is A>B>C>D. It is ovbious the combination of CP and EP gives exellent frequency characteristics of impedance.

PROCESS OF POLYPYRRROLE POLYMERIZATION

We observed how polypyrrole was filled in micropores having 1-2μm diameter on aluminum foil through the chemical oxidative polymerization and the electrochemical polymerization by SEM. Figure 2 shows SEM photographs.

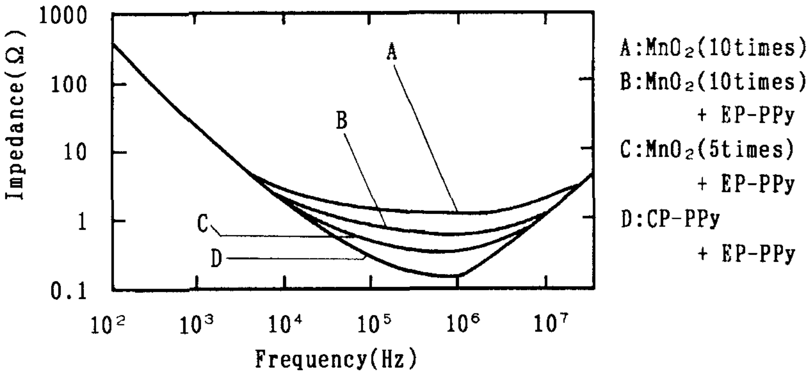

FIGURE 1 Frequency characteristics of impedance for various tantalum electrolytic capacitors.

The photographs of the surface show many polypyrrole particles of which diameter is under 0.1μm were prepared by the CP, then electrochemical polymerized polypyrrole grew on them. After ten minutes the diameter was 0.5-1μm and after 60 minutes the borders of the particles were not clear to be like a layer.

The right side shows section of the aluminum foil in which both horizontal and vertical etching pits present. The photographs of the section show the inside surface of the pits were covered with polypyrrole thin layer of fine particles through the CP. The electrochemical polymerized polypyrrole grew on and filled micro-pores. The thickness of the polypyrrole can be observed from the horizontal pits and is 0.4μm after 60 minutes, which is thinner than the surface one because a migration rate of pyrrole monomer into the pits is slow. Therefore, as the electrochemical polymerization exceeds an appropriate period, the electric resistance increases.

DOPANT SPECIES AND CAPACITOR CHARACTERISTICS

It is well known the conductivity and thermal stability of polypyrrole depend on the dopant species. We examined these effects on tantalum electritical capacitors by preparing with various supporting electrolytes. The initial characteristics are shown in Table II. Both the ESR and tanδ of the cpacitors using BDS^{2-}(benzenedisulfo-

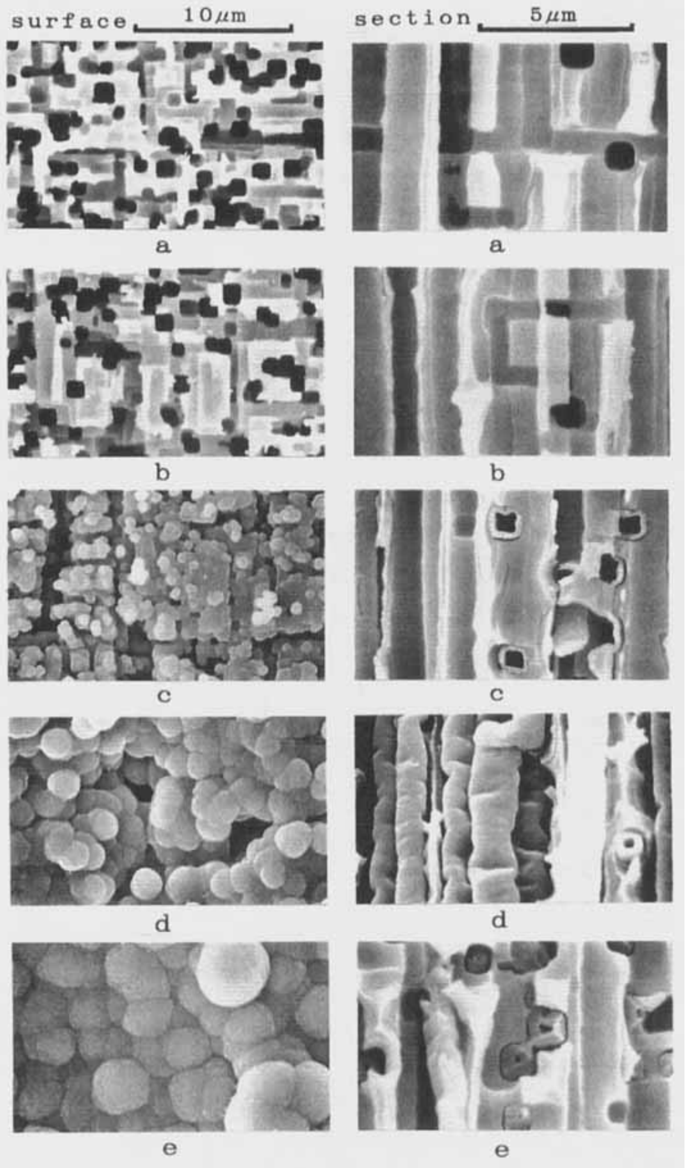

FIGURE 2 SEM photographs of process of polypyrrole polymerization.

left side: surface, right side: section
a: after forming
b: after 1 time of chemical oxidative polymerization
c: after 10 minutes of electrochemical polymerization
d: after 30 minutes of electrochemical polymerization
e: after 60 minutes of electrochemical polymerization

TABLE II Effects of dopant species on capacitor characteristics.

Dopant	Capacitance (μF)	tanδ (%)	ESR (mΩ)
ClO_4^-	1.36	0.94	733
BF_4^-	1.19	0.85	481
PF_6^-	1.39	2.36	2063
TFA^-	1.30	1.60	815
BDS^{2-}	1.36	0.70	350
TsO^-	1.38	0.80	185

nate) and PTS^-(paratoluenesulfonate) as the dopants are superior to othes, such as PF_6^-,TFA^-(trifluoroacetate),ClO_4^-,BF_4^-. Figure 3 shows characteristics as a function of time at 105℃ atomosphere.

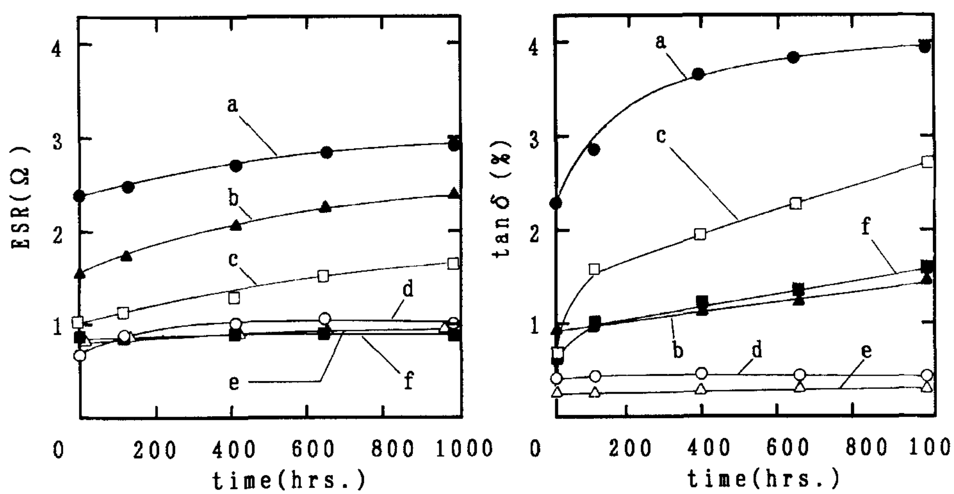

FIGURE 3 Electrical characteristics of polypyrrole tantalum capacitors as a function of time.

a: PF_6^- b:TFA^-(trifluoroacetate) c:ClO_4^-
d:BDS^{2-}(benzenedisulfonate) e:TsO^-(paratoluenesulfonate)
f:BF_4^-

There is little change of slope with time in the case of using the aromatic sulfonate dopants. On the contrary, other dopants show rapid increases as the time proceeds. These results coincide with the reported thermal stabilities of polypyrrole films[7].

In addition, there were no problem in practical through soldering tests at 260℃, roading life tests at 125℃ and moisuture life tests at 85℃ and 85%RH.

FREQUENCY CHARACTERISTICS OF IMPEDANCE

The frequency characteristics of impedance of an aluminum electrolytic capacitor employing polypyrrole (PA) and a tuntalum electrolytic capacitor employing polypyrrole (PT) are shown in Figure 4 in comparision with those of an aluminum electrolytic capacitor employing liquid electrolyte (CE) and a tantalum electrolytic capacitor employing MnO_2 solid electrolyte (CS). The frequency characteristics of impedance at high frequency regions of capacitors employing polypyrrole (PA, PT) are exellent superior to those of CE and CS, and are comparable to that of film capacitor.

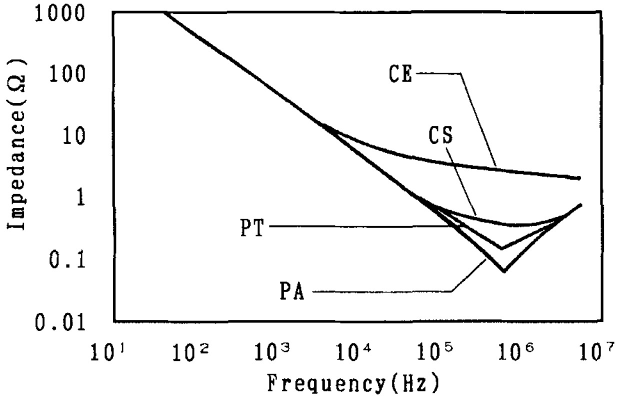

FIGURE 4 Frequency characteristics of impedance for various electrolytic capacitors.

PA: polypyrrole type aluminum electrolytic capacitor
PT: polypyrrole type tantalum electrolytic capacitor
CE: liquid type aluminum electrolytic capacitor
CS: MnO_2 type tantalum electrolytic capacotor

CONCLUTION

New type of aluminum and tantalum capacitors employing only polypyrrole as solid electrolytes were depeloped, which reveal exellent frequency and temperature characteristics.

A chemical oxidative polymerized polypyrrole is superior to a pyrolytic prepared manganese dioxide as a conductive pre-coating layer. Aromatic sulfonate dopants give thermal stabilities and excellent capacitor characteristics.

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