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Modification of Anodized Aluminum Film by Hyperbranched Poly(siloxysilane)s in Conductive Polymer Aluminum Solid Electrolytic Capacitor

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An aluminum solid electrolytic capacitor, using poly(3,4-ethylenedioxythiophene) (PEDOT) as a counter electrode, was prepared with hyperbranched poly(siloxysilane)s (HBPSi) to improve an interface of aluminum oxide and PEDOT. Capacitance and equivalent series resistance (ESR) were significantly improved comparing to those without HBPSi.

Conductive polymer aluminum solid electrolytic capacitors have attracted considerable attention because of their extremely low impedance at high frequencies and reliability.[1–8] The capacitor has various applications in high performance digital equipment. Conductive polymers, such as polypyrrole (PPy) or PEDOT, are used as a counter electrode for aluminum oxide in these capacitors. The properties of the capacitor are strongly influenced by not only the conductivity of the polymers but the affinity between the aluminum oxide and the conductive polymers. It has been reported that addition of vinyltrimethoxysilane or γ-aminopropyltriethoxysilane to PPy electrolyte solution improves electrical properties such as capacitance and dissipation factor of tantalum solid electrolytic capacitors.[9] This could be due to the effect of the siloxane derivatives of organic and inorganic hybrid materials that play a role of affinity between the PPy and the tantalum oxide.

HBPSi are of interesting candidates for a new class of organic and inorganic hybrid materials. Because they have a dendritic structure consists of Si–O and hydrocarbon segments with a large number of organic terminated groups that can be easily modified to various functional groups and would play a significant role of connecting with an organic layer. HBPSi, therefore, offers intriguing possibilities for the materials especially as coatings, adhesives, and surfactants.[10–12]

In this paper, we report that modification of aluminum anodized film by HBPSi increases contact area with PEDOT, and improves the capacitor's characteristics, such as capacitance and ESR.

HBPSi with vinyl terminated groups was synthesized by the hydrosilylation of AB_2 monomer, 1,5-divinyl-1,1,3,5,5-pentamethyltrisiloxysilane, in the presence of platinum catalyst at room temperature for 3 h in bulk (Figure 1). Furthermore, we also used crosslinked type HBPSi that prepared with the crosslinking reaction of the resulting HBPSi and 1,1,3,3-tetramethyldisiloxane as a cross linker in the presence of platinum catalyst in toluene at room temperature for 1 h. Molecular weight of as prepared and cross linked polymers was determined by using gel permeation chromatography (GPC) with polystyrene standard. The linear polysiloxanes, vinyl-terminated polydimethylsiloxanes (PDMSi) with two different molecular weights (Shinetsu Polymer DMT-V35, $M_n = 770$ and 49500), were used for the reference samples to HBPSi. Ethylenedioxythiophene (EDOT) and iron *p*-toluenesulfonate were purchased from H. C. Starck and used without further purification.

Figure 2 shows a schematic view of the fabricated device of aluminum solid electrolytic capacitor. An electrochemically etched aluminum foil (5 mm × 190 mm × 100 µm) with lead wire was anodized at 4 V to form an aluminum oxide dielectric layer. Thickness of the oxidized layer was approximately 6 nm. The aluminum foils and separators were wound together to form an element. The element was immersed into a solution of the HBPSi in hexane and then dried at 90 °C for 1 h. The surface of the aluminum oxide film based on the aluminum foil was coated with the conjugated polymer of PEDOT by dipping in a mixture of butanol solution containing EDOT and iron *p*-toluenesulfonate followed by heating at 150 °C to complete chemical poly-

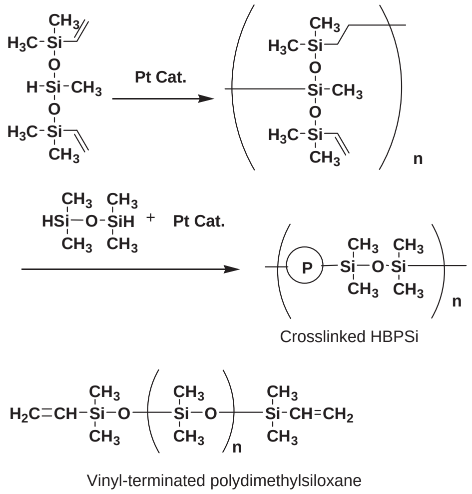

Figure 1. Structure and abbreviation of employed chemical compounds.

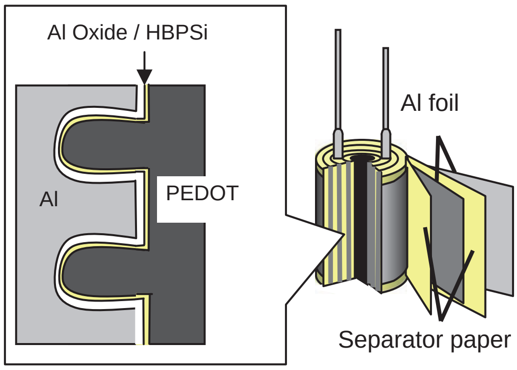

Figure 2. Schematic view of the fabricated device.

Table 1. Summary of the effect of HBPSi on capacitance and ESR

	M_n	M_w / M_n	Cap. [μF/120 Hz]	ESR [mΩ/100 kHz]
No treatment			240	23
HBPSi (as prepared)	5600	1.8	410	8.5
Cross-linked HBPSi	16000	2.6	630	5.6
PDMSi(A)	770		180	23
PDMSi(B)	49500		120	24

merization.[13,14] Capacitance and ESR were measured by using precision LCR meter 4284A (Agilent).

Table 1 summarizes the effect of HBPSi and vinyl-terminated polydimethylsiloxane (PDMSi) on capacitance and ESR of the capacitors. These values are results using 3% solution in hexane. The precoating of HBPSi increased capacitance to 410 μF and decreased ESR to 8.5 mΩ for the capacitors. Moreover, when crosslinked HBPSi that has apparent large molecular weight of 1.6×10^4 were introduced into the aluminum oxide/PEDOT interface, the capacitor performance was remarkably improved. It is noted that no modification effects of vinyl-terminated linear PDMSi were observed. The reason seems to be that the linear PDMSi has less interaction with the aluminum oxide surface compared with HBPSi because of high hydrophobicity.

Capacitance is expressed by the following Eq 1:

$$C = \mathcal{E}S/d \qquad (1)$$

where $\mathcal{E}$, S, and d are permittivity, surface area, and thickness of the aluminum oxide film on the etched aluminum foil, respectively. Since these parameters are not change in this experiment, variation in the capacitance reveals change in area of aluminum oxide film contacts with PEDOT. ESR shows both the resistance of aluminum oxide/PEDOT interface and the PEDOT. Hydrogen bonding between Si–O in HBPSi and Al–OH on the aluminum oxide surface could be formed, on the other hand, the vinyl group and the methyl group have an affinity by hydrophobic interaction. Therefore, it is considered that introducing HBPSi, which contains a large number of vinyl terminated groups, into the aluminum oxide/PEDOT interface enlarges the contact area by improving adhesion for the interface.

Figure 3 shows changes in capacitance and ESR as function of concentration of HBPSi and crosslinked HBPSi in hexane. Capacitance increased with increase of the concentration. On the other hand, ESR decreased with increase of the concentration up to 1.0 wt %, and no great improvement was observed in higher concentration than 1.0 wt %. Crosslinked HBPSi also showed the almost similar behavior. The scarce adhesions of a hydrophilic aluminum oxide film and hydrophobic PEDOT are considered to be the main causes of characteristics degradation of the capacitors. When small quantity of the hydrophobic HBPSi (<1 wt %) is coated on the aluminum oxide surface, the HBPSi coating should be ununiform and exists in the shape of an island. For these concentrations, since the surface coverage increased dramatically, the capacitance and the ESR were improved. In concentration region higher than 1.0 wt %, the HBPSi coating seems to be homogeneous on the aluminum oxide. Therefore, no changes of capacitance and ESR were observed at the high concentration region of HBPSi.

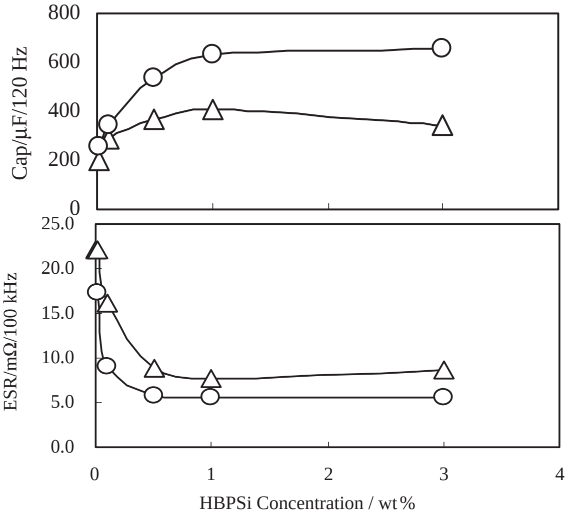

Figure 3. Comparison of capacitance and equivalent series resistance for capacitors using PEDOT: (△) HBPSi with Mn of 5700, (○) crosslinked HBPSi with Mn of 16000.

In conclusion, we demonstrated that introduction of HBPSi and crosslinked HBPSi into the aluminum oxide/PEDOT interface is effective in improving the characteristics of the aluminum solid electrolytic capacitor as compared with linear polymer, vinyl terminated polydimethylsiloxanes. Although the crosslinked HBPSi was more effective than as prepared HBPSi, both showed same behavior for the relation between concentration and the characteristics for the capacitors.

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