Short communication

The effects of hyperbranched poly(siloxysilane)s on conductive polymer aluminum solid electrolytic capacitors

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Abstract

An aluminum solid electrolytic capacitor, using poly-(3,4-ethylenedioxythiophene) (PEDOT) as a counter electrode, was prepared with hyperbranched poly(siloxysilane)s (HBPSi) that has a large number of vinyl groups to improve the interfacial properties between aluminum oxide and PEDOT. Capacitance and equivalent series resistance (Rs) were significantly improved compared to untreated oxide film and vinyl terminated polydimethylsiloxane coated interfaces. From electrochemical measurement of the withstand voltage, damage to the oxide film from chemical polymerization of PEDOT was less with the HBPSi treatment. Frequency characteristics and electrical conductivity measurements of the polymer indicated that the resistance inside the etched porous layer was greatly reduced. These results show that the HBPSi pre-coating layer inhibited degradation of the oxide film by chemical polymerization of PEDOT and the conductivity of PEDOT in the etched porous oxide layer, and also enlarges the contact area by improving interfacial adhesion.
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1. Introduction

Conductive polymer aluminum solid electrolytic capacitors have attracted considerable attention because their extremely low impedance at high frequencies and reliability [1–7]. Application for these types of capacitors includes high performance digital equipment, such as liquid crystal displays, personal computers, and game consoles. The further improvement of these devices requires higher performance from the capacitor.

Conducting polymers, such as polypyrrole (PPy) and poly (3,4-ethylenedioxythiophene) (PEDOT), are used as counter electrodes for aluminum oxide in these capacitors. The properties of capacitors are influenced by not only conductivity of the polymers but the interface between the aluminum oxide and the polymers. In the electrochemical polymerization of PPy, it is very important to prepare an electro-conductive layer on the insulating oxide film, such as using soluble polyaniline [8] or MnO_2 [1]. It has been reported that addition of vinyltrimethoxysilane and gamma-aminopropyl triethoxysilane to the PPy electrolyte solution improves electrical properties such as capacitance and dissipation factor for tantalum solid electrolytic capacitors [9]. It is believed that vinyltrimethoxysilane acts as a coupling agent between the PPy main chain and the vinyl group.

Hyperbranched poly(siloxysilane)s (HBPSi) are interesting candidates as a new class of organic–inorganic hybrid materials. HBPSi has a dendritic-like structure consisting of Si–O and hydrocarbon segments that terminate into a large number of organic groups. The organic segments can be easily transformed to various functional groups to promote interaction with an organic layer. HBPSi, therefore, offers intriguing possibilities for materials especially, as a coating, adhesive, or surfactant [10–12].

Our strategy for improving the characteristics of a conductive polymer aluminum solid electrolytic capacitor is to improve the interface between aluminum oxide and PEDOT

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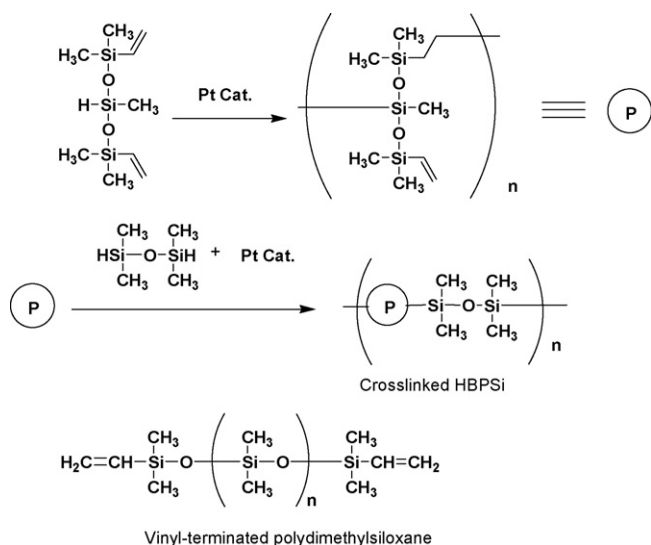[1] Tel.: +81 3 5734 2429; fax: +81 03 5734 2875.

Fig. 1. Structures and reaction schemes.

Fig. 2. Aluminum solid electrolytic capacitor (wound type): schematic.

by hyperbrunched polymer. We have already reported that the characteristics of the capacitor are improved by hyperbranched Poly(siloxysilane)s [13]. Here in, we report the improving mechanism of Rs and capacitance of the capacitors by evaluating an aluminum oxide films and PEDOT, frequency characteristics, and voltage–current characteristics.

2. Experimental

2.1. Preparation of vinyl terminated HBPSi

1,5-Divinyl-1,1,3,5,5-pentamethyltrisiloxysilane and 1,1,3,3-tetramethyldisiloxane were purchased from Tosco and Sigma–Aldrich, respectively. Both chemicals were used without further purification.

HBPSi with vinyl terminated groups was synthesized by the hydrosilylation of neat AB$_2$ monomer, 1,5-divinyl-1,1,3,5,5-pentamethyltrisiloxysilane, in the presence of platinum catalyst at room temperature for 3 h (Fig. 1). Furthermore, we also prepared a crosslinked type HBPSi from the resulting HBPSi and 1,1,3,3-tetramethyldisiloxane as a cross linker in the presence of a platinum catalyst in toluene at room temperature for 1 h. Molecular weights of HBPSi and crosslinked HBPSi were determined by gel permeation chromatography (GPC) against a polystyrene standard.

The linear polysiloxanes, vinyl terminated polydimethylsiloxanes (PDMSi) with two different molecular weights (Shinetsu Polymer DMT-V35, Mn = 770 and 49,500), were used as received.

2.2. Capacitor fabrication

Ethylenedioxythiophene (EDOT) and iron p-toluenesulfonate were purchased from H. C. Starck and used without further purification. Fig. 2 shows a schematic view of the fabricated device, an aluminum solid electrolytic capacitor. An electrochemically etched aluminum foil (5 mm × 190 mm × 0.1 mm)
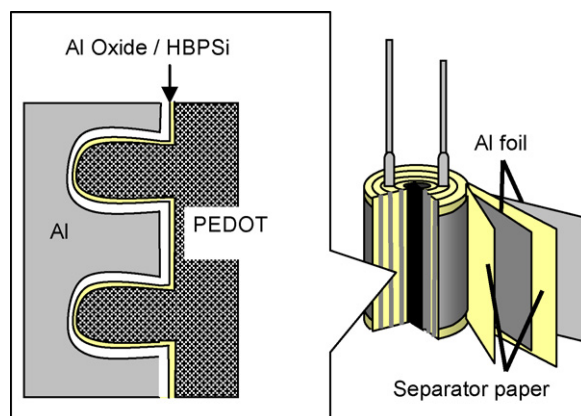
with lead wire was anodized at 4 V to form an aluminum oxide dielectric layer. Thickness of the oxidized layer was approximately 6 nm. The aluminum foils and separators, which is a polyethylene terephthalate nonwoven fabric, were wound together to form an element. The element was immersed into a solution of the HBPSi in hexane and then dried at 90 °C for 1 h. The surface of the aluminum oxide film on the aluminum foil was coated with the PEDOT by dipping into a butanol solution containing EDOT and iron p-toluenesulfonate then heating at 150 °C to polymerize. The element was sealed in an aluminum can identical to that used for electrolytic aluminum capacitors. A 3 V dc current was then applied for 60 min at 130 °C to reduce the leakage current.

2.3. Evaluation of the capacitor

Capacitance and ESR were measured by a precision LCR meter 4284A (Agilent).

In order to evaluate damage to the aluminum oxide dielectric layer by oxidative polymerization, the element was carefully removed from the capacitor to measure withstand voltage of the aluminum oxide dielectric layer. The element was heated at 500 °C for 4 h to decompose the PEDOT. The electrode was then removed from the element, rinsed in dilute nitric acid, and washed with the water. Withstand voltage test of the electrode was carried out in an ammonium adipate aqueous solution at 25 °C with a constant current of 1 mA cm^{-2}.

PEDOT was prepared on separator paper coated with HBPSi under the same conditions as the capacitor to evaluate the effect of HBPSi on conductivity of PEDOT. Conductivity was measured with 4-pin probe resistivitymeter (MCP-T600, MITSUBISHI CHEMICAL Corp.).

3. Results and discussions

3.1. Comparison to linear PDMSi

The effect of HBPSi and vinyl terminated polydimethylsiloxane (PDMSi) on capacitance and ESR of the capacitors is summarized in Table 1. The HBPSi pre-coating increased capacitance to 410 μF and decreased ESR to 8.5 mΩ. Addi-

Table 1
Comparison of characteristics for the capacitors using HBPSi, cross linked HBPSi and PDMSi

	Mn	Mw/Mn	Capacitance (μF)[a]	Rs (mΩ)[b]
HBPSi (as prepared)	5,600	1.8	240	8.5
Cross linked HBPSi	16,000	2.6	410	5.6
PDMSi(A)	770		180	23
PDMSi(B)	49,500		120	24
Untreatment			240	23

All samples prepared from hexane at 3 wt% concentration.
  [a] Measurements were carried out at 120 Hz.
  [b] Measurements were carried out at 100 kHz.

tionally, when crosslinked HBPSi with an apparent molecular weight of 1.6×10^4 or greater was introduced into the aluminum oxide/PEDOT interface, the capacitor performance was remarkably improved. It is noted that vinyl terminated linear PDMSi decreased capacitance and had no effect upon Rs. The reason seems to be that the linear PDMSi has less interaction with the aluminum oxide surface compared with HBPSi because of fewer functional groups to promote interaction.

3.2. The effect of coating conditions

Changes in capacitance and ESR as a function of coating concentration are shown in Fig. 3. Capacitance increased logarithmically with the increasing in the concentration. Conversely, ESR decreased logarithmically with increasing in the concentration reaching an apparent plateau at 1.0 wt%. The crosslinked HBPSi was more effective than non-crosslinked HBPSi, though both showed improvements over non-treated samples.
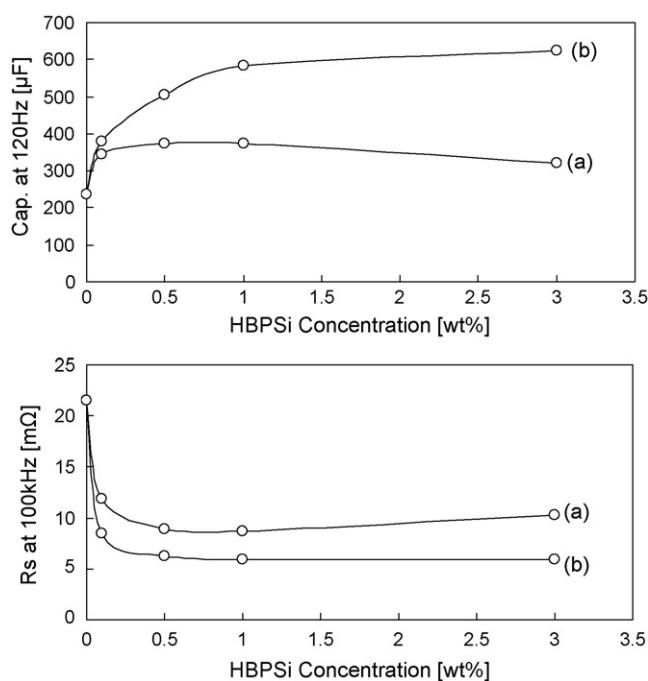

Fig. 3. Comparison of capacitance and equivalent series resistance (Rs) for capacitors using PEDOT: (a) non-crosslinked HBPSi (Mn of 5700) and (b) crosslinked HBPSi (Mn of 17,000).
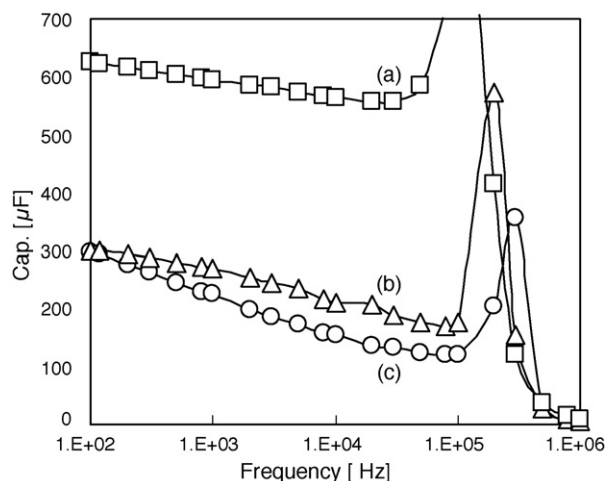

Fig. 4. Frequency dependence of capacitance for the capacitors treated with: (a) crosslinked HBPSi (3% concentration), (b) non-crosslinked HBPSi (3% concentration), (c) untreated.

3.3. Capacitance

The frequency dependence of capacitance in the capacitors fabricated from non-crosslinked, crosslinked HBPSi and the untreated is shown in Fig. 4. The effects on the capacitance were observed over low to high frequency, which implies better coverage by PEDOT on the dielectric surface than without treatment.

The results of the withstand voltage measurements are shown in Fig. 5. The voltage increase in the initial stages indicates the relative number of defects in the oxide dielectric film, and the equilibrium voltage (VF) corresponds to the thickness of the oxide layer.

Electric charge attained under constant voltage is described by the following equation:
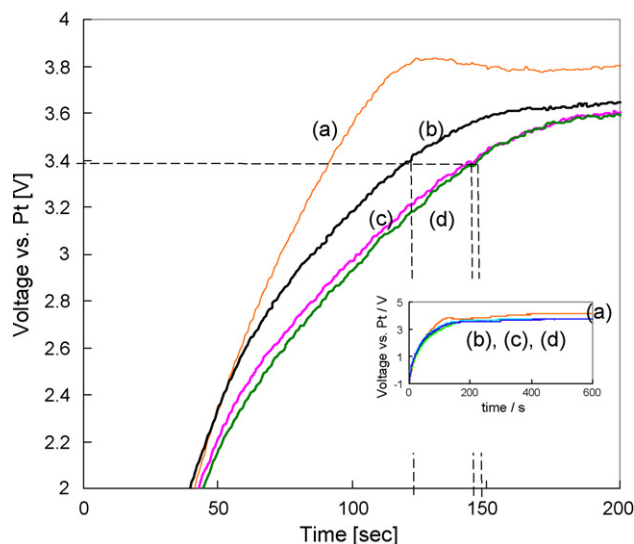
$$Q = It \tag{1}$$

Fig. 5. Withstand voltage measurements in 15% aqueous ammonium adipate at 30 °C at a current density of 1 mA cm^{-2}. Before PEDOT polymerization, (b) after PEDOT polymerization with crosslinked HBPSi (1% concentration), (c) crosslinked HBPSi (0.1% concentration), and (d) untreated.

Table 2
A comparison of tan δ and Re for the capacitors

Sample	Q (C cm^{-1})
Before PEDOT polymerization	4.6×10^{-2}
Crosslinked HBPSi (1.0% concentration)	6.1×10^{-2}
Crosslinked HBPSi (0.1% concentration)	7.4×10^{-2}
Untreatment	7.3×10^{-2}

where Q, I and t are the electric charge quantity, electric current and time, respectively. The calculated results for Q values at 3.4 V are shown in Table 2. The dielectric oxide film treated with crosslinked HBPSi at a 1% concentration performs the best after PEDOT polymerization, suggesting that the number of defects is smaller.

However, the VF for untreated and 0.1% concentration after PEDOT polymerization is nearly identical as seen in the Fig. 5 inset. All values are about 0.3 V lower than the before the PEDOT polymerization. This indicates that the thickness of the oxide dielectric film is not influenced by the presence or lack of any treatment.

Capacitance (C) is expressed by the following equation:

$$C = \varepsilon \frac{S}{d} \tag{2}$$

where ε, S and d are permittivity, surface area and thickness of the dielectric oxide film on the etched aluminum foil, respectively. As described above, d after PEDOT polymerization is not influenced by the presence or lack of a pre-treatment and ε is a constant.

Therefore, any changes in capacitance are directly, related to the change in contact area. Ergo, the improvement in capacitance by crosslinked HBPSi (1% concentration) corresponds to an increase in contact area.

Iron p-toluenesulfonate is used as an oxidizer and a dopant. This can react with hydroxyl groups and/or absorbed water on the aluminum oxide surface, to form $Fe(OH)_3$ and p-toluenesulfonic acid (pTSA). The pTSA can cause the defects and the surface dissolution of the dielectric layer. It is believed that the HBPSi prevents the dielectric oxide films from damage, thus increasing the contact area due to improved adhesion of the interface between the dielectric oxide film and the PEDOT.

3.4. Equivalent series resistance

Frequency dependence of equivalent series resistance (Rs) for capacitors coated with 1% crosslinked HBPSi, 1% HBPSi and untreated are shown in Fig. 6. The Rs for equivalent circuit of the capacitor shown in Fig. 7 is expressed by the following equation [8,14]:

$$Rs = \frac{\tan \delta}{2\pi f C} + Re \tag{3}$$

where tan δ, f, C and Re are the dissipation factor of the dielectric oxide film, frequency, capacitance, and resistance due to the conducting polymer both inside and outside of the etching pits, respectively. The relationship between Rs and $1/2\pi f C$ is
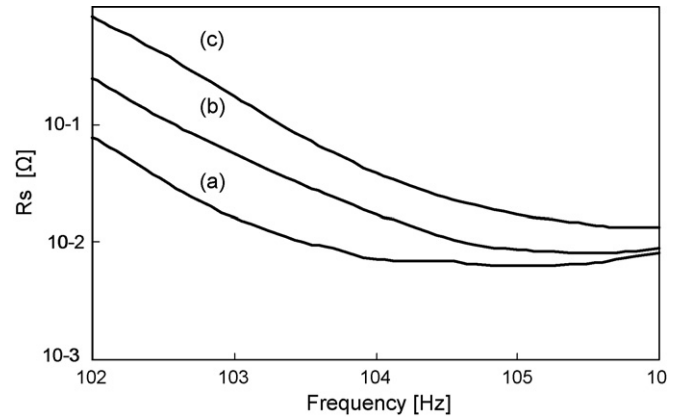

Fig. 6. Frequency dependence of equivalent series resistance (Rs) for capacitors coated with (a) crosslinked HBPSi (1% concentration), (b) HBPSi (1% concentration) and (c) untreatment.
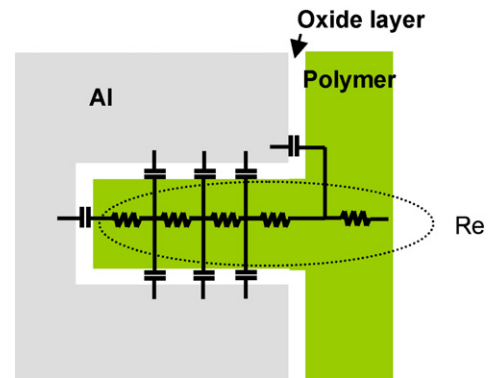

Fig. 7. The equivalent circuit for a capacitor with an etched aluminum surface.

linear at low frequencies, where the slope of the line gives tan δ. Re is determined by extrapolating to infinite frequency where $1/2\pi f C = 0$. A comparison of tan δ and Re for the capacitors with and without HBPSi and those without are shown in Table 3.

The capacitor using crosslinked HBPSi exhibits the lowest tan δ and Rs. This is likely due to the inhibited damage of the dielectric oxide film from the chemical polymerization of EDOT. Re is a function of the PEDOT within and outside of the etching pit, i.e. on the separator papers between the electrodes. The conductivity of PEDOT formed on separator papers coated with various concentrations of crosslinked HBPSi is shown in Fig. 8. Significant improvement in the conductivity is not observed, indicating that the lower Re is associated with the PEDOT in the etching pits.

In general, resistance is inversely proportional to contact area, which is proportional to capacitance. Therefore, Rs should be in

Table 3
A comparisons of tan δ and Re for the capacitors

	tan δ	Re
Crosslinked HBPSi	0.045	0.044
As prepared HBPSi	0.026	0.012
Untreatment	0.14	0.13

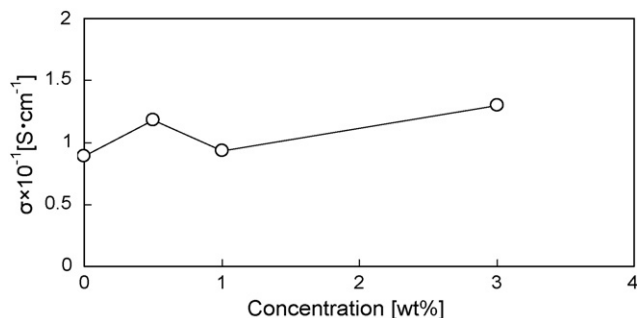Both of crosslinked and as prepared HBPSi sample are prepared from 1.0% concentration.

Fig. 8. Conductivity of PEDOT formed on separator paper coated with various concentrations of crosslinked HBPSi.

inversely proportional to capacitance. The relationship between Rs and capacitance for several capacitors fabricated under various HBPSi treatment conditions are shown in Fig. 9. The inverse proportion between the Rs and the capacitance is observed independently of the treatment conditions. From these results, the improvement in Rs is caused by an increase in contact area between PEDOT and oxide dielectric layer. This result agrees with the capacitance improvement. The pre-coating with HBPSi prevents the oxide dielectric film from degrading by *p*TSA, thus expanding the contact area with PEDOT. This enables improvement of the capacitors characteristics, such as capacitance and Rs.

3.5. Current–voltage curves

The current–voltage curves for the capacitors using crosslinked HBPSi are shown in the Schottky plots (Fig. 10). The current increases linearly with increasing voltage, similar to conventional solid electrolytic capacitors. The slope of crosslinked HBPSi from 3% is the same as 0.1% and untreated. It indicates that the amount of crosslinked HBPSi does not form insulating layer at the interface between the oxide dielectric film and PEDOT.

In order to evaluate harm to HBPSi (Mn = 5000) by oxidative polymerization, HBPSi was mixed with excess of the butanol solution containing iron *p*-toluenesulfonate then heating at 150 °C. The reaction product was extracted from the solidified products with ether and purified by rinsing with water giving HBPSi (Mn = 770) in 18% yield. The residual solid was rinsed with methanol giving gelatinous HBPSi.
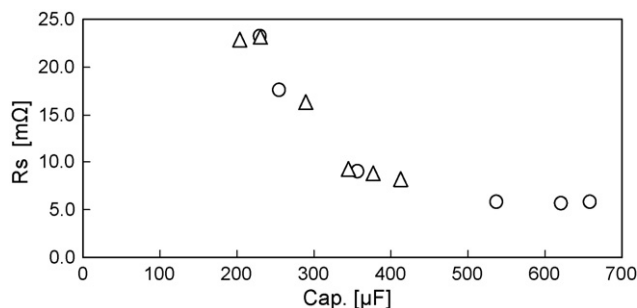

Fig. 9. Relationship between Rs and capacitance. Data from Fig. 3 graphs replotted against each other.
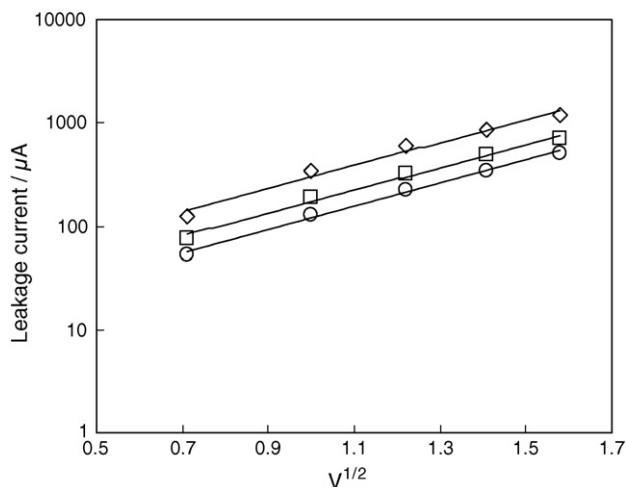

Fig. 10. Current–voltage curves for capacitors pre-treated with (○) crosslinked HBPSi (3% concentration), (□) crosslinked HBPSi (0.1% concentration) and (△) untreatment.

The damage to the oxide dielectric film by *p*TSA is considered to be the main cause of performance degradation in capacitors. As shown in Fig. 3, when a small quantity of HBPSi (<1 wt%) is coated on the aluminum oxide surface, the HBPSi coating is likely incomplete and patchy. Although the HBPSi, which contains siloxane bonds, is decomposed by *p*TSA, a portion of gelled HBPSi remains on the oxide dielectric surface. As shown in Figs. 3 and 4, the inhibiting effect of the HBPSi on the oxide layer is partial. For these concentrations, the capacitance and ESR were improved since the increase of HBPSi is able to more completely cover the surface. In concentrations higher than 1.0 wt%, the HBPSi coating seems to be uniform on the aluminum oxide. Since excessive HBPSi on the surface may be decomposed by acid, a very thin HBPSi layer seems to remain without forming an insulating layer. Therefore, no changes of capacitance and ESR in Fig. 8 and the slope of the current–voltage curves in Fig. 9 were observed at the high concentrations region of HBPSi. The crosslinked HBPSi, which has a larger molecular weight (Mw = 1.6×10^4), is less susceptible to the effects of acidic decomposition than the as prepared HBPSi (Mw = 5000). This should enable a significant improvement in the characteristics of the capacitors.

4. Conclusions

Conductive polymer aluminum solid electrolytic capacitors using PEDOT as a counter electrode were fabricated with a pre-coating layer consisting of HBPSi bearing a large number of vinyl groups. Introduction of HBPSi or crosslinked HBPSi onto the aluminum oxide/PEDOT interface was effective in improving the performance of the capacitor as compared with linear, vinyl terminated polydimethylsiloxanes. In particular, the crosslinked HBPSi showed excellent improvement in capacitance and equivalent series resistance.

The withstand voltage measurements of the used electrode foils and the other analysis showed that HBPSi inhibits the damage to the oxide dielectric layer from the chemical polymer-

ization of PEDOT, thus increasing the contact area by improved adhesion of the interface between the dielectric oxide film and the PEDOT. The increase in contact area is considered to be the main factor in the improvement of capacitor performance.

From this study, it is shown that not only an improvement of the electro-conductivity of conductive polymers but also an enhancement of affinity between the conductive polymer and oxide dielectric films is important for improving capacitor performance. HBPSi, which can be functionalized with other chemical groups, in addition to vinyl groups, has potential as an effective material in the improvement of interfacial properties.

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