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Short communication

One-pot synthesis of polypyrrole film on an aluminum oxide layer by electropolymerization in the presence of ammonium borodisalicylate in acetonitrile

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Abstract

This paper describes how one-pot preparation of polypyrrole (PPy) on Al_2O_3 layer in an aluminum solid capacitor could be achieved by electropolymerization of pyrrole (Py) in acetonitrile with small amounts of water, using ammonium borodisalicylate (ABS) as a new electrolyte. The effects of monomer and electrolyte concentrations, current density, and polymerization temperature on the PPy formation on Al_2O_3 layer in aluminum solid are also discussed. Polymerization occurred smoothly to give PPy on the Al_2O_3 layer under the following conditions: [ammonium borodisalicylate] = 0.02 M, [Py] = 0.1 M, and polymerization temperature = −42 °C, current density = 10 mA cm^{-2}. The normalized capacitance, the C_p/C_0 value of capacitor fabricated, reached more than 0.9, indicating that the porosity and surface of the Al_2O_3 layer are filled up and covered with PPy. The Raman spectra of the PPy film showed that the peak assignable to C=C backbone stretching shifted to a lower wave number of 1585 cm^{-1}. This indicates formation of the film with well-conjugated C=C backbone. The SEM micrograph of PPy on Al_2O_3 layer showed a closely packed globular morphology. These results indicate that the new electrolyte, ABS, has an excellent ability to form PPy film directly on Al_2O_3 surface by electropolymerization.

Keywords: Polypyrrole; Ammonium borodisalicylate; Electropolymerization; Aluminum solid-state capacitor

1. Introduction

The development of electrically conductive polymers has now led to making available various electronic circuits for practical application in a number of industrial systems. Many studies have focused on the synthesis of various conductive polymers [1]. Among these, polypyrrole (PPy) has attracted the attention of many, because the electrochemically polymerized PPy is known for its high conductivity and good physical strength. Many factors influence the chemical and physical properties of PPy film on metal surface, including the nature and concentration of supporting electrolyte, monomer concentration, the property of solvent, and the conditions of electropolymerization process such as temperature, potential, and current density.

The direct electrodeposition of PPy in aqueous solutions on active metals such as aluminum and zinc was difficult due to the involvement of the undesirable metal oxidation in parallel with PPy formation. Several techniques have been reported for overcoming the disturbance that obstructs PPy film formation on active metal. For the preparation of PPy/Al_2O_3/Al solid state capacitor, etching Al surface to enable formation of aluminum oxide layer and pretreatment of conducting layer such as chemically synthesized PPy or MnO_2 on the aluminum oxide layer are essential process prior to electrochemical polymerization of Py [2–10]. Alternatively, utilizing disodium salt of 4,5-dihydroxy-1,3-benzenedisulfonic acid has been suggested, because this acts as an electron transfer mediator to reduce the deposition potential of PPy on aluminum and aluminum alloy [11,12]. Furthermore, simultaneous formation of Al_2O_3 dielectric layer

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and PPy polymer electrolyte on Al foil has been investigated, utilizing the chemical reactions operated in the system [13].

The advantage of synthesizing conductive polymers in organic solvents over electrodeposition of PPy layer from aqueous solution is, in general, the high solubility of monomer, which might be effective in preparing the polymer layer with a high rate, and the suppression of dissolution of active metals. The deposition of PPy films on Al, Ti, Pt, Ni, Zn, and Zn–Pb–Ag has been studied, and their morphologies, mechanical properties, and conductivities have been reported [14–17]. However, to our knowledge, few studies have been reported on the synthesis of PPy film by electropolymerization of Py in acetonitrile (AN) on Al_2O_3 layer. In this work, we report on how efficiently we could achieve the direct formation of PPy on an aluminum oxide layer by electrochemical polymerization of PPy in AN using a new supporting electrolyte, ammonium borodisalicylate (ABS).

2. Experimental method

2.1. Materials

Salicylic acid, citric acid, tartaric acid, phthalic acid, boric acid, pyrrole (Py), acetonitrile (AN), ammonium adipate, and ammonium borodisalicylate (ABS) were purchased (pure grade or extra pure grade) from Tomiyama Chemical and used without further purification.

2.2. Preparation of PPy/Al_2O_3/Al film

A typical example was as follows. A surface of etched aluminum foil (size: 0.5 cm × 0.8 cm, thickness: 100 μm) was anodized to form an insulating oxide layer at 14 V in a 10 wt% ammonium adipate aqueous solution. A 0.5 cm × 0.4 cm section of anodized aluminum foil was immersed into Py monomer ([Py] = 0.1 mol dm^{-3}) in AN solution containing 0.085 mol dm^{-3} ABS electrolyte and small amounts of water (850–1000 ppm). Electrochemical polymerization was carried out by the constant current density method (10 mA cm^{-2}) for 15 min at −42 °C. The aluminum plate and the anodized etched aluminum foil were used as the counter electrode and the working electrode, respectively. To fabricate a capacitor, the PPy layer on the aluminum foil was coated with colloidal carbon and silver paint, followed by molding with epoxy resin after the cathode and the anode leads were attached.

2.3. Measurements

The concentration of water in AN was measured by the Carl Fischer's method. The surface morphologies of the PPy film on the aluminum foil were examined by scanning electron microscopy (JEOL, JSM5310). The capacitance of aluminum solid electrolytic capacitor was measured at 120 Hz (C_p) with an LCR meter 4263B (Hewlett-Packard). The value was compared to the capacitance (C_0) of an aluminum oxide layer filled with a 30 wt% sodium acetate aqueous solution. The relative capacitance, C_p/C_0 value, was used as a measure of functionality of the capacitor prepared in this study. The equivalent series resistance (ESR) of the aluminum solid electrolytic capacitor was measured at 100 kHz, using a LCR meter 4263B (Hewlett-Packard). Raman spectra were recorded with a JRS-FT 6500N microscopic Raman spectrometer employing a 785 nm laser beam and InGaAs detector with 4 cm^{-1} resolution. PPy films were washed repeatedly with methanol and dried at room temperature. Thermogravimetric analysis (TGA) of PPy film was carried out with a TGD-5000VH (ULVAC-RIKO) at a heating rate of 10 °C min^{-1} under an air atmosphere. The conductivity of PPy film doped with ABS was measured using a standard four-probe method (Kyowa Riken K-705RS). The film thickness was obtained from the difference between before and after electropolymerization of PPy on the Al_2O_3/Al, using Mitutoyo thickness meter ID-C112A. The error in thickness measurement was less than 10%.

Table 1
Electropolymerization of pyrrole on the surface of Al_2O_3/Al

No.	Electrolyte system	mol dm^{-3}	Film	ESR (mΩ 100 kHz^{-1})
1	Ammonium borodisalicylate	0.015	Yes	51.0
2	Salicylic acid	0.015	No	–
3	Salicylic acid	0.030	Yes	50.0
	Boric acid	0.015		
4	Citric acid	0.015	No	–
5	Citric acid	0.030	Yes	147.1
	Boric acid	0.015		
6	Tartaric acid	0.015	No	–
7	Tartaric acid	0.030	Yes	376.1
	Boric acid	0.015		
8	Phthalic acid	0.015	No	–
9	Phthalic acid	0.030	No	–
	Boric acid	0.015		
10	Sodium 4-toluenesulfonate	0.015	No	–
11	Sodium 2-naphthalenesulfonate	0.015	No	–

Synthesis conditions of PPy: [Py] = 0.1 M, current density, 10 mA cm^{-2}; polymerization temperature, −42 °C.

3. Results and discussion

As has been reported in previous papers [18,19], the presence of a small amount of water for electropolymerization of Py in AN is known to bring about the favorable effects on the polymerization rate, film conductivity, and film morphology. In this experiment, small amounts of water (850–1000 ppm) were added to the polymerization system.

3.1. Effect of electrolyte on electropolymerization of pyrrole

Attempts to prepare directly PPy film on the Al_2O_3 layer have been made by using a combination of various hydroxyl organic compounds and boric acid as an electrolyte.

Table 1 summarized the effect of electrolytes used in this study on the electropolymerization of Py in AN at −42 °C. When [salicylic acid]/[boric acid] = 2 was used, the polymerization occurred smoothly to cover Al_2O_3 layer. The ESR value of the film was found to be 50 mΩ, suggesting that the film with high conductive ability adhered to the Al_2O_3 layer. For the 2:1 citric acid/boric acid and 2:1 tartaric acid/boric acid electrolyte systems, PPy films were prepared but their ESR values were considerably high as compared to that obtained from the salicylic acid/boric acid electrolyte system, indicating that the performance of film formed on the Al_2O_3 layer is affected by the structure of hydroxyl organic groups. The mixture of salicylic acid and boric acid is known to form spontaneously a tetravalent, tetrahedral boron complex, which is expected to act as a useful electrolyte for the polymerization of Py. In fact, no formation of PPy was observed for the phthalic acid/boric acid electrolyte system, because it was impossible for two COOH groups in phthalic acid molecule to participate in the boron complex formation. From these results, it appears that the complex formed from salicylic acid and boric acid functions efficiently as an electropolymerization mediator. In accordance with this argument, the addition of ammonium borodisalicylate (ABS) that has been alternatively prepared instead of the 2:1 salicylic acid/boric acid electrolyte system conduced to the formation of PPy film on the Al_2O_3 layer, which has almost the same value of 51 mΩ. The filling up of porosity in and covering on the Al_2O_3 layer with PPy are necessary to construct high performance PPy/Al_2O_3/Al capacitors. The results suggest that ABS aptly assists in the penetration of Py into the porosity of the Al_2O_3 layer, which makes it possible to fill up the porosity with PPy, although the detailed role of ABS remains to be solved.

The mechanism of electropolymerization of Py is very complex; whether PPy film forms on Al_2O_3 layer or not depends on various factors such as electrolyte concentration, monomer concentration, current density, and polymerization temperature. We studied in detail the electropolymerization of Py using ABS electrolyte in AN with small amounts of water.

3.2. Effect of ABS concentration

As shown in Fig. 1, the C_p/C_0 value, the relative capacitance of the PPy/Al_2O_3/Al system to one of the standard

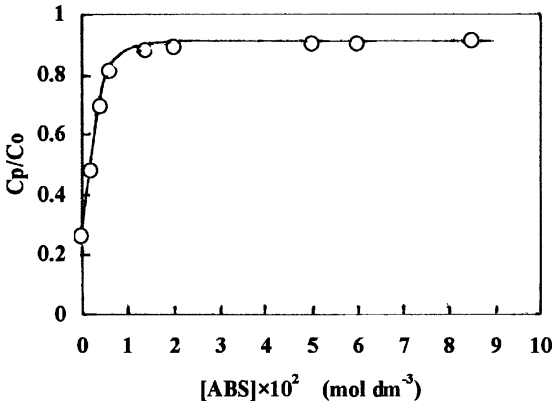

Fig. 1. Effects of ABS concentration on C_p/C_0. Synthesis conditions of PPy: [Py] = 0.1 mol dm^{-3}; [ABS] = 3.5 × 10^{-4} to 0.088 mol dm^{-3}, polymerization temperature, −42 °C; current density, 10 mA cm^{-2}.

30 wt% sodium acetate aqueous solutions, increased with increasing [ABS]/[Py], and became a constant value above [ABS]/[Py] = 0.2. The C_p/C_0 value being 0.9 at [ABS]/[Py] = 0.2 suggests that almost the entire surface of Al_2O_3 layer is covered by PPy film. In addition, the high value implies that the polymer film obtained had high conductivity and that it adhered to Al_2O_3 surface. Apparently, ABS acts as both a supporting electrolyte and a dopant in the PPy film.

Raman spectroscopy is a useful method to evaluate the structure of PPy [20,21]. The characteristic Raman peaks of PPy were observed in the 1000–1150 cm^{-1} range, 1300–1430 cm^{-1} range, and at *ca.*1600 cm^{-1}, which are assignable to C–H in-plane deformation, ring stretching, and C=C backbone stretching, respectively. The most important peak is the one at *ca.* 1600 cm^{-1}, which is closely related to the conjugation length of PPy. As shown in Fig. 2, the PPy film obtained from electropolymerization of Py in the presence of ABS showed the double peaks at 1081 and 1052 cm^{-1}, the other double peaks at 1369 and 1232 cm^{-1}, and the peak at 1587 cm^{-1}. The appearance of the downshift peak at 1587 cm^{-1} suggests the development of PPy conjugated system in the film. In agreement with this, the film has a conductivity of 10^2 S cm^{-1} at room temperature,

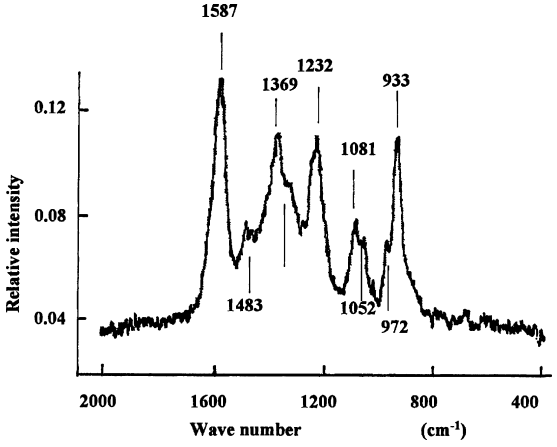

Fig. 2. Raman spectra of PPy film obtained from the electropolymerization of Py in the presence of ABS.

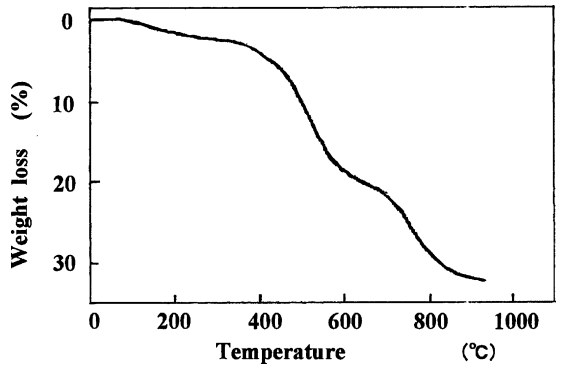

Fig. 3. TGA curve of PPy with ABS dopant in air. Scan rate, 10 °C min^{-1}.

which corresponds to the conductivity obtained from PPy doped with anthraquinone-2-sulfonic acid [22].

The type of dopant anion used during polymerization has a profound influence on the stability of PPy film due to the change of the interchain and conformation of polymer caused by the interaction between PPy and the dopant anion. As shown in Fig. 3, PPy film containing ABS as dopant was thermally stable, and the thermal behaviors exhibited features similar to those of the PPy-sulfonate systems [23].

3.3. Effect of monomer concentration

The effect of Py monomer concentration in the range of 0.025 to 0.5 mol dm^{-3} was studied by electrochemical polymerization of Py onto an oxide layer of an aluminum etched foil working electrode at a constant current of 10 mA cm^{-2} in an AN solution containing 0.05 mol dm^{-3} ABS at −42 °C. As shown in Fig. 4, the C_p/C_0 value reached 0.85 when the concentration of pyrrole was about 0.1 M and then decreased with increasing concentration of pyrrole. The fact that the electropolymerization even at a relatively low concentration of Py ([Py] = 0.03 mol dm^{-3}) gave PPy film indicates that ABS is an effective mediator for the polymerization. For such low concentrations, however, the surface was not fully covered with PPy films, as evidenced by the SEM photographs (Fig. 5). At high concentrations of Py ([Py]>0.15 mol dm^{-3}), the formation of PPy with unfavorable

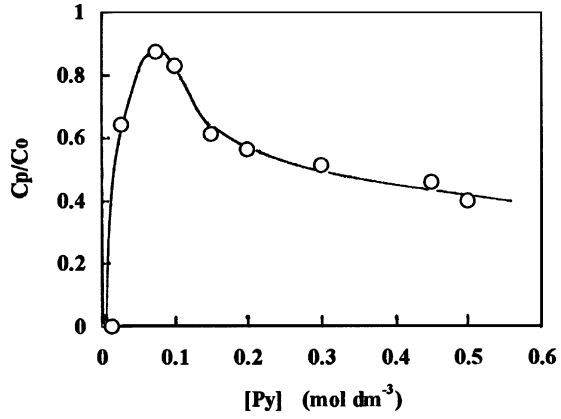

Fig. 4. Effects of Py concentration on C_p/C_0. Synthesis conditions of PPy: [ABS] = 0.05 mol dm^{-3}; polymerization temperature, −42 °C; current density, 10 mA cm^{-2}.

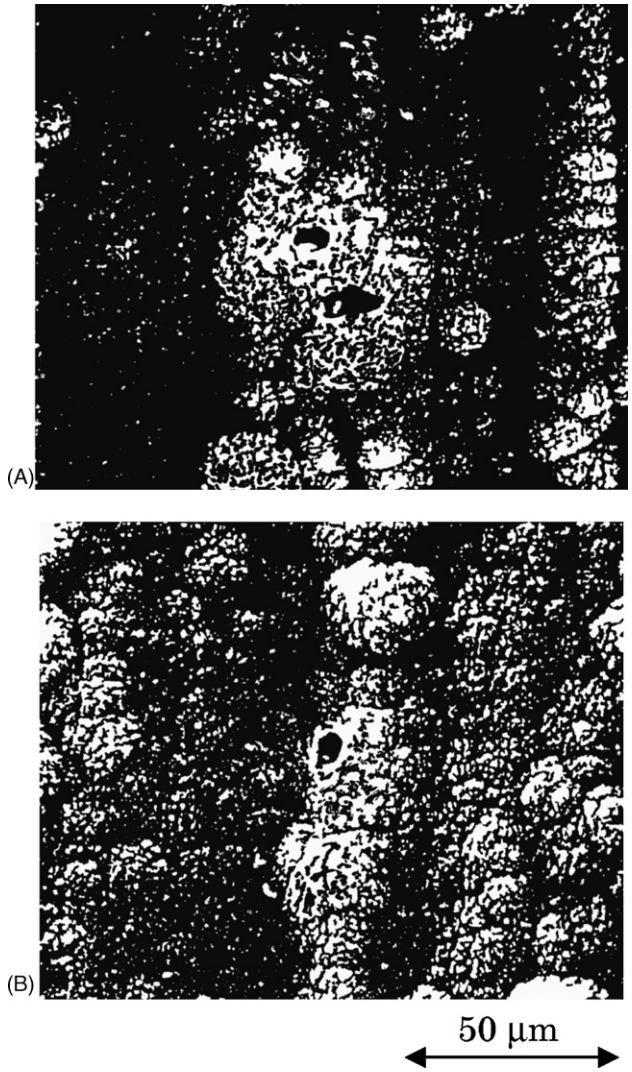

Fig. 5. SEM photographs of PPy obtained at: (A) [Py] = 0.03 mol dm^{-3} and (B) = 0.2 mol dm^{-3}. Synthesis conditions are described in Fig. 4.

nodular structure was observed, suggesting that rapid growth of the polymer was operative. It seems likely that the rapid growth of PPy also brings about the existence of unfilled porosity with PPy in the Al_2O_3 layer, *i.e.*, the porosities are covered with PPy before filling up with the polymer, which causes lowering of C_p/C_0 value. Thus, the concentration of Py giving rise to a suitable PPy film is highly limited.

3.4. Effect of current density

The coating and corrosion performance of Al_2O_3/Al are greatly influenced by applied potential. Electropolymerization of pyrrole was carried out by applying different current densities ranging from 7 to 35 mA cm^{-2}. No electropolymerization occurred below 5 mA cm^{-2} but a PPy film with fairly uniform on Al_2O_3/Al formed when current density of 7 mA cm^{-2} was applied. As shown in Fig. 6, the increase in current density increased the ESR value of capacitors, probably due to rapid and rough growth of PPy. For electrochemical polymerization of Py, especially in an aqueous solvent, the formation of poly-

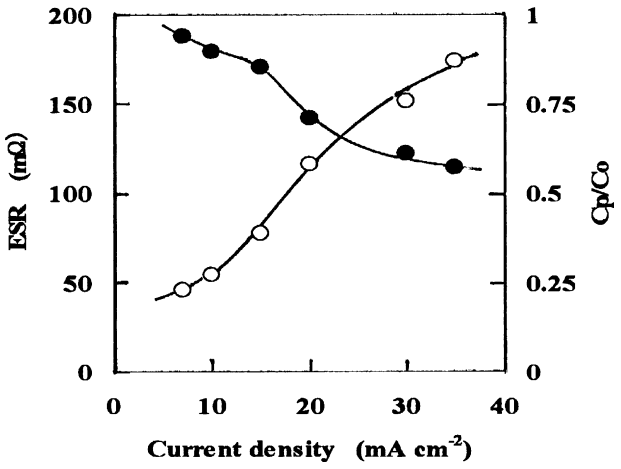

Fig. 6. Effects of current density on ESR (◯) and C_p/C_0 (●). Synthesis conditions of PPy: [Py] = 0.1 mol dm^{-3}; [ABS] = 0.025 mol dm^{-3}; polymerization temperature, −42 °C.

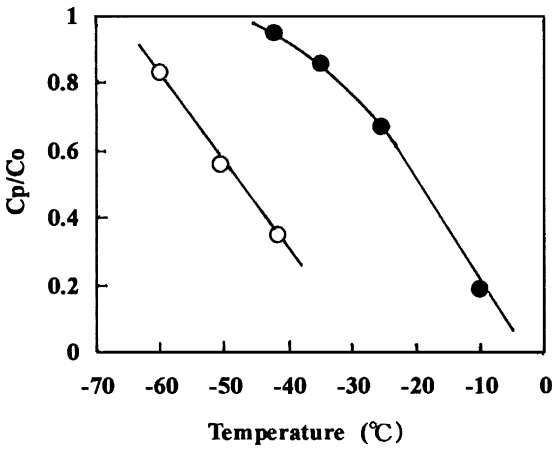

Fig. 8. Effects of polymerization temperature in AN (●) and 7:3 AN-acetone (◯) on C_p/C_0. Synthesis conditions of PPy: [ABS] = 0.025 mol dm^{-3}, polymerization temperature, −42 °C. Current density, 10 mA cm^{-2}.

mer layer often competes with the growth of Al_2O_3 layer, and if the latter process is faster, the film does not form on the Al_2O_3 layer. To confirm whether Al_2O_3 layer was growing in the electropolymerization system using ABS or not, electrochemical treatment was carried out under the same conditions except for the absence of monomer. No significant change of relative potential values (V_t/V_0) of a solution of AN containing ABS and water was observed for 3 min, where V_0 and V_t denote the voltage observed at 5 and t sec after supplying a current density (10 mA cm^{-2}), respectively. Although further supplying a current density brought about the increase of V_t/V_0 value, for the electropolymerization system the polymerization of Py initiated to form PPy on the Al_2O_3 within 3 min. Therefore, it appears that the growth of Al_2O_3 layer under the polymerization conditions can be ruled out.

Fig. 7 shows the relationship between the thickness of the PPy film and the amount of charge passed during electrochemical polymerization at two different current densities, 10 and 30 mA cm^{-2}. The thickness of the PPy film on Al_2O_3 surface might be proportional to the amount of the charge above the critical point. In both cases the accumulation of PPy on Al_2O_3 surface was observed after *ca.* 1 C cm^{-2} supply. This suggests that *ca.* 1 C cm^{-2} is required for the formation of PPy film on Al_2O_3 surface. In other words, Py polymerized predominantly in the holes of the film etched rather than on the surface of Al_2O_3. At 30 mA cm^{-2}, the PPy film grew rapidly and obtained with 4 μm thickness around *ca.* 2 C cm^{-2}. The C_p/C_0 value of the film, however, showed a low level of 0.6 (Fig. 6), indicating that PPy was unevenly distributed as nodules without covering the surface of Al_2O_3.

In contrast to this, in electropolymerization of pyrrole with 10 mA cm^{-2} current density, Py polymerized with a slow rate. At 4 C cm^{-2}, the thickness of PPy was *ca.* 2 μm, which was one-fourth of the thickness of PPy obtained at 30 mA cm-^{2} current density. The relatively thinness of the film suggests that the surface of Al_2O_3 was coated homogeneously with the conducting polymer. In fact, the C_p/C_0 of the film obtained at 10 mA cm^{-2} current density reached a high value of 0.9.

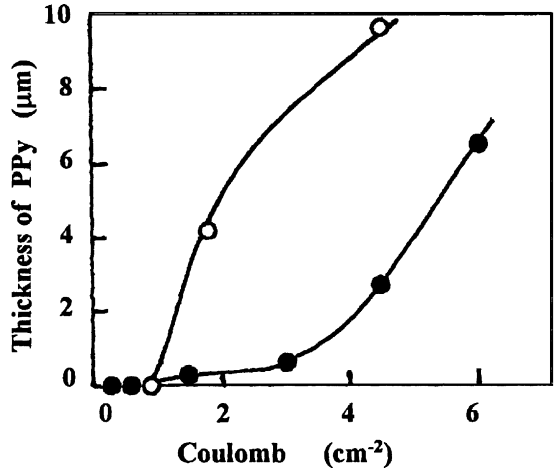

Fig. 7. Effects of current density on the thickness of PPy film. Synthesis conditions of PPy: [Py] = 0.1 mol dm^{-3}; [ABS] = 0.025 mol dm^{-3}, polymerization temperature, −42 °C; current density, 10 mA cm^{-2} (●) and 30 mA cm^{-2} (◯).

3.5. Effect of temperature

Fig. 8 shows the relationship between (C_p/C_0) and the temperature of electrochemical polymerization of Py monomer (0.1 mol dm^{-3}) and ABS (0.025 mol dm^{-3}) at 10 mA cm^{-2} in AN solution. The C_p/C_0 value increased with decreasing the polymerization temperature, and reached 0.95 at −42 °C. Reflecting this, the ESR value decreased from 250 mΩ at −10 °C to 49 mΩ at −42 °C. Fig. 9 shows that the polymer obtained at −42 °C is characterized by the presence of a closely packed nodular morphology, in contrast to the film synthesized at −10 °C where PPy appears as a cauliflower-like cluster. The nodules become smaller as the polymerization temperature decreases. Therefore, it may be concluded that capacitors having PPy films prepared at as low temperature as possible acquire the greatest capacitance. It would be of interest to investigate if the film that forms at a lower temperature than −42 °C can have a high C_p/C_0 value or not. Electrochemical polymerization of

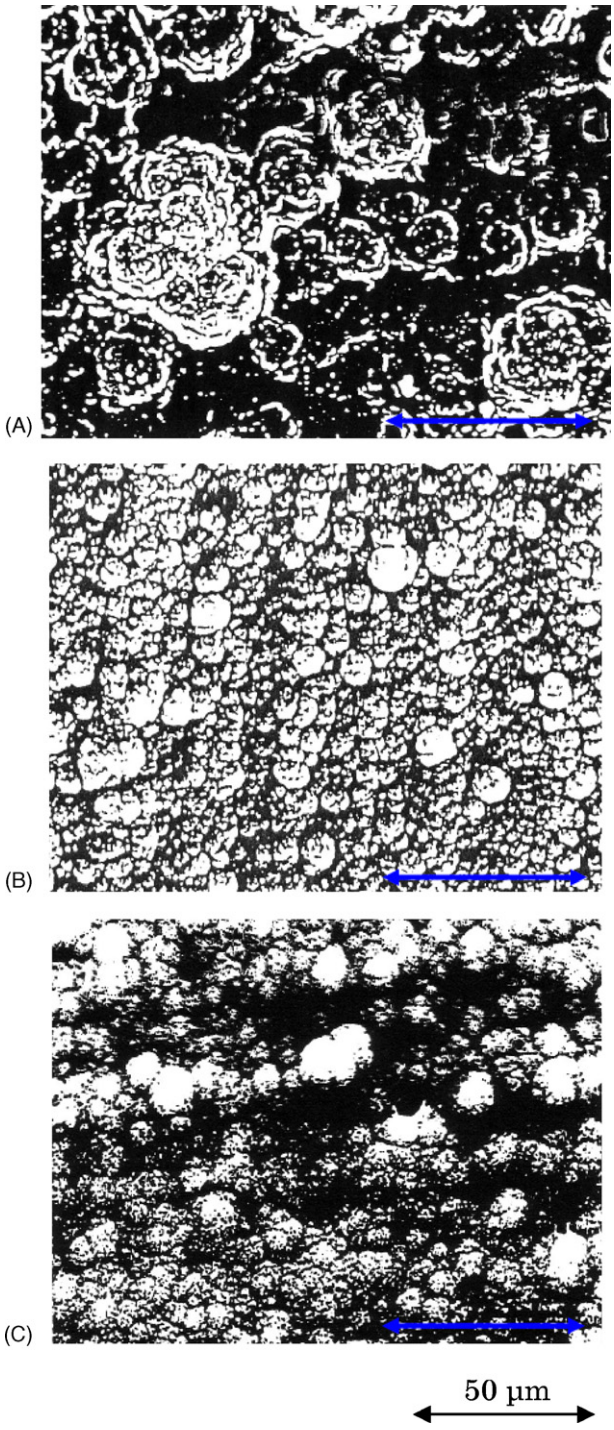

Fig. 9. SEM photographs of PPy obtained at: (A) −10 °C, (B) −42 °C in AN and (C) −60 °C in 7:3 AN-acetone. Synthesis conditions of PPy: [Py] = 0.1 mol dm^{-3}; [ABS] = 0.025 mol dm^{-3}; current density, 10 mA cm^{-2}.

Py at −50 and −60 °C was carried out using a mixture of 7:3 AN-acetone containing 0.1 mol dm^{-3} Py and 0.025 mol dm^{-3} ABS at a constant current density of 10 mA cm^{-2}, although the presence of acetone might affect the polymerization pathways. Fig. 9 shows that the C_p/C_0 values of capacitor with PPy film formed at −60 °C were qualitatively the same as those of the PPy film formed at −30 °C.

4. Conclusion

The presence of ABS, which acts as an electrolyte for electropolymerization of PPy, opens the door to direct formation of polypyrrole in AN on Al_2O_3. The polymer film formed on Al_2O_3 was affected by monomer concentration, ABS concentration, and current density. The results showed that the following condition is suitable for the preparation of PPy film: [ammonium borodisalicylate] = 0.02 M, [Py] = 0.1 M, and current density = 10 mA cm^{-2}. Polymerization temperature is also critical in preparing an aluminum solid electrolytic capacitor with excellent characteristics. The lower the polymerization temperature, the better would be the formation of polypyrrole film. Thus, the use of ABS makes it possible to efficiently prepare PPy coated solid-state electrolytic capacitors.

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