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Electropolymerization Conditions for Producing Insulator Polypyrrole Films

Tetsuya OSAKA, Toshiyuki MOMMA, and Himeko KANAGAWA
Department of Applied Chemistry, School of Science and Engineering,
Waseda University, 3-4-1 Okubo, Shinjuku-ku, Tokyo 169

By using the electropolymerization of pyrrole from aqueous solutions of Na_2CO_3 or $NaHCO_3$, flat and pinhole-less insulating films were obtained due to the self-leveling and self-saturation effects. The influences of the supporting electrolyte and of the additive (N-methylpyrrole) to the NaOH polymerization solution were also investigated to produce the insulating PPy films having some different properties.

In recent years, many researchers have been found that the electropolymerized polypyrrole (PPy) formed from acidic or neutral solution has high electroactivity and conductivity,[1] and the active film becomes electroinactive and also insulating when dipping it into the alkaline solution.[2] We already reported that the electroinactive PPy film can be directly formed from the NaOH polymerization solution,[3] and the metal/insulator /metal (MIM) type diode using the PPy film as the insulator shows non-linear resistor[3] and works well as the switching element of the liquid crystal cell.[4] In this paper, we introduce the conductance variation of the electroinactive PPy films deposited from alkaline solution with several supporting electrolytes, and the effect of an additive of N-methylpyrrole (MePy) to the polymerization solution.

The insulating PPy films were formed on indium tin oxide (ITO) substrates from the aqueous solution of 0.25 mol dm^{-3} pyrrole monomer by using the constant potential electro-oxidizing polymerization at 1.5 V vs. Ag/AgCl. Three aqueous solutions of 0.2 mol dm^{-3} Na_2CO_3, 0.2 mol dm^{-3} $NaHCO_3$ and 0.01 mol dm^{-3} NaOH containing pyrrole were used, and their pH values are 12.01, 11.51 and 8.22, respectively. In order to examine the effect of the introduction of methyl group to the PPy chain, one mmol dm^{-3} MePy was added as an additive to the polymerization solution using NaOH electrolyte. The thickness and the morphology of the PPy film were determined by the contact profile meter and secondary electron microscope (SEM) observation. The structure of the PPy molecule was checked by the microscopic FT-IR spectroscopy. Construction and measurement of the MIM device were done as similar as described before.[3]

With applying 1.5 V vs. Ag/AgCl in the polymerization solution containing Na_2CO_3 or $NaHCO_3$, polymerized products were formed on the ITO substrates. The molecular structure of the PPy polymerized for 60 min from the polymerization solution using various electro-

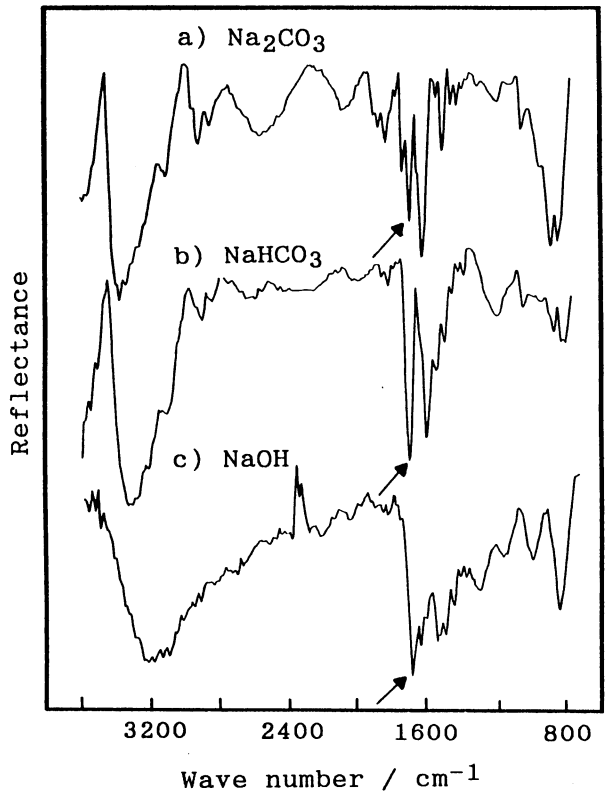

Fig. 1. FT-IR reflection spectra of electropolymerized PPy films obtained at 1.5 V vs. Ag/AgCl for 60 min. The supporting electrolytes of the polymerization solutions were Na_2CO_3, $NaHCO_3$ and NaOH for a), b) and c), respectively.

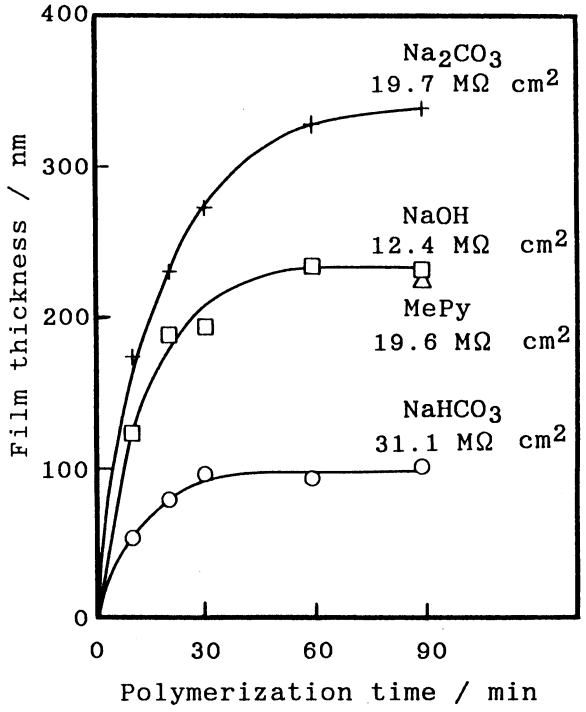

Fig. 2. The relationship between the film thickness and the electrolysis time at 1.5 V vs. Ag/AgCl. The supporting electrolytes of the polymerization solutions are indicated in the figure. The film resistances under 0.5 V application to the MIM device are also shown in the figure.

lytes was determined by the FT-IR absorption as shown in Fig. 1. Very little difference can be observed in each FT-IR spectrum. A strong absorption peak at 1697 cm^{-1} can be observed clearly in each spectrum (see arrow), which was attributed to the C=O stretching vibration. The C=O structure supports that the carbonyl group is generated in the PPy chains during the film formation in each aqueous solution, as is previously pointed out.[3] The formation of carbonyl group can be due to the attack of nucleophilic ions of hydroxide, carbonate or hydrogencarbonate to the generated radical at α- or β-carbon of the pyrrole unit. The formation of the carbonyl group in the PPy molecule means the shortening of the π conjugation length, and causes the inactivation of the PPy molecule and thus the high resistance of the film.[3] The FT-IR results show that not only from the strong alkaline NaOH solution, but also from a weak alkaline solution of pH=8.22 the inactivated PPy film can be obtained by selecting the supporting electrolyte.

The thickness of the films is shown in Fig. 2 as a function of the polymerization

time, where the resistance values in the figure are determined with the MIM devices using the 90 min polymerized film under 0.5 V application. The thickness of each film increases with the polymerization time and seems to be saturated at a certain value. These films are confirmed to be a flat morphology from the SEM observation. The saturation of the film thickness and morphology flattened mechanism is explained by the electropolymerizing formation of insulating films. After forming the insulating film onto the conducting substrate, the pinhole areas of film are continuously buried by insulating film and the final film becomes pinhole-less conditions. Namely, the pinhole areas and heterogeneous areas of the film are leveled by the selective flux of the polymerization current to the less-resistive parts. The resistance of each film shows an interesting phenomenon. With varying the supporting electrolyte of the polymerization solution, the resistance shows no relation with the pH value of the solution. By referring to the film obtained from pyrrole and NaOH solution, the film from the NaOH solution adding MePy has higher resistance. Considering that, in the case of fully electroactive film, the conductance of the poly-MePy film is lower than that of PPy film due to the introduction of methyl group to the pyrrole unit,[6] the depression of the film conductivity with adding a small amount of MePy to the polymerization solution may come from the co-polymerization of Py and MePy. In the case of using Na_2CO_3 the resistance of the film was lifted up by the increase of the film thickness. Using $NaHCO_3$ as the supporting electrolyte during polymerization, the resulting film has the highest resistance though its thickness was the thinnest. This suggests that during the polymerization under the application of high potential, the PPy molecule is highly

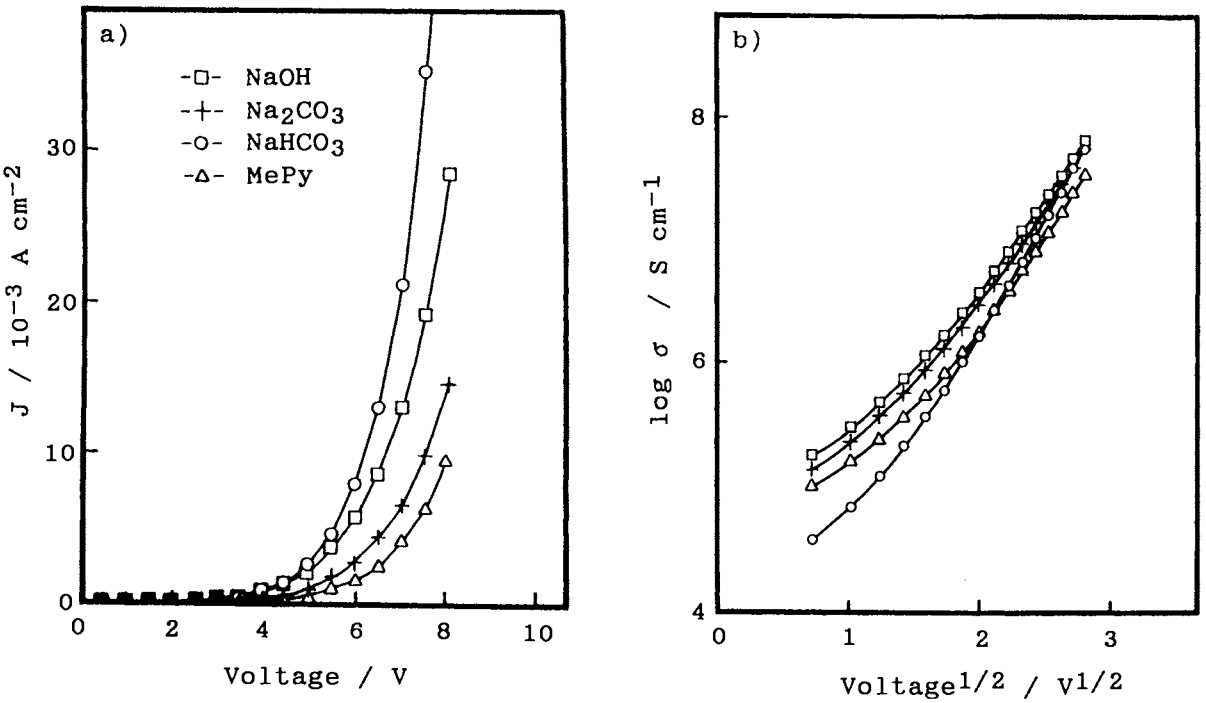

Fig. 3. Electrical characteristics of the MIM devices using various insulating PPy films polymerized for 60 min. The applied voltage was stepped with 0.5 V to 8 V.

oxidized and easily attacked by not only hydroxide but also the nucleophilic hydrogencarbonate anion.

Figure 3 shows the electric characteristics of the MIM elements using four types insulating PPy films under stepping the applied voltage. In Fig. 3a, all devices demonstrate the switching performances well, and each element has the alternate threshold voltage and non-linearity. Fig. 3b reveals those profiles more clearly. Each plot was aligned linearly and it suggests that the Poole-Frenkel effect dominates the conducting mechanism in all the films as previously reported for the PPy film from NaOH solution.[5] The inclination of the line reflects non-linear current-voltage profile, while the resistance of the film governs the threshold voltage. These results show that the variation of the film properties can be selected by the polymerizing conditions of the electroinactive PPy film.

In conclusion, not only from a strong alkaline solution but also from a weak alkaline solution of $NaHCO_3$, insulating PPy film was obtained by the application of high potential. The PPy films formed from NaOH, $NaHCO_3$ or Na_2CO_3 solution have a wide variation of conductivity and film thickness. This polymerization method of insulating film shows a self-leveling and self-saturation effects of the film thickness due to the high resistance across the film. The coexistence of MePy during the insulating PPy formation causes the increase of the film resistance.

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