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An Application of Polypyrrole Films Electropolymerized in NaOH Aqueous Solution to Non-linear MIM Devices

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Thin films of electroinactive polypyrrole(PPy) were electropolymerized in NaOH aqueous solutions on ITO(indium tin oxide) electrode. The PPy films were used at as-prepared condition without undoping process. The metal-insulator-metal(MIM) structure was fabricated by sputtering ITO on the PPy films to give ITO/PPy/ITO devices. The devices showed non-linear and symmetric I-V characteristics, where the currents sharply increased at ca. ±5 V.

An MIM(Metal-Insulator-Metal) device is practically used as a switching device for driving liquid crystal(LC) and expected to realize a larger area LC display because of its simple manufacturing process.1) Many studies of organic insulating layers for MIM devices have been reported, for example, LB(Langmuir Blodgett) films,2) evaporated polymer films such as polyethylene,3) and so on. With regard to an electropolymerized film as an insulator, we first reported the I-V characteristics of the MIM device using the undoped poly-N-methylpyrrole(PMPy) film.4) Since the as-prepared PMPy film containing ClO_4^- anion is conducting, it has to be undoped to obtain an insulating state for non-linear characteristics. If an electroinactive film can be obtained directly at as-prepared condition, it is more useful for its application. Electroinactive films such as polyphenol5) and polyaniline prepared in non-acidified conditions6) have already been reported, however, we failed to get a suitable film from these polymers concerning the adherence to ITO electrode. Then we found that an inactive PPy film electropolymerized in a NaOH aqueous solution is suitable for the insulator owing to its adherence and low conductivity. The preparation of the nonconducting PPy in the NaOH solution has only been stated briefly by Murthy et al. without detailed conditions.7) In this letter, we will report the proper conditions of preparing the PPy film in the basic solution for the application to the insulator of MIM device and refer to its I-V characteristics.

The electrolytes were 0.1 mol dm^{-3}(M) and 0.01 M NaOH aqueous solutions containing 0.25 M pyrrole. The PPy films were formed on ITO electrode (ca. 400 nm) by constant potential electrolysis at 1.5 V vs. Ag/AgCl. ITO/PPy/ITO devices were fabricated by sputtering ITO(ca. 60 nm) on the PPy films which were washed in water and dried with the stream of argon gas after electropolymerization. The pattern profile of the MIM devices used here was the same as in the previous experiments,[4)] where the hole sizes for polymer layer were 100, 300, 500, 700, 1000 μm in diameter. In the experiments, the device of each hole size gave the same results of I-V characteristics, and thus all the results were represented with the devices of 300 μm diameter. I-V characteristics were measured between ±10 V by 0.5 V step.

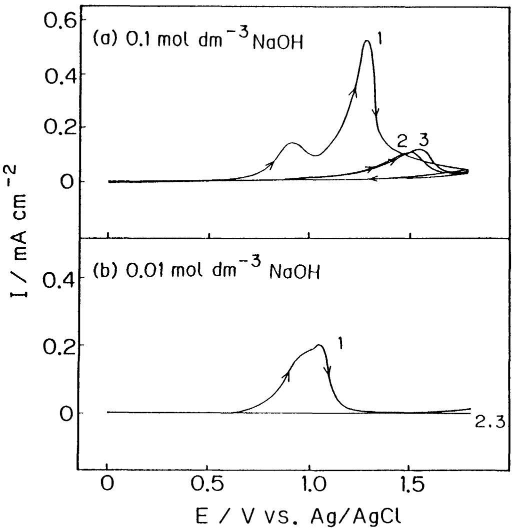

Fig. 1. Cyclic voltammograms at 10 mV s^{-1} in NaOH aqueous solutions containing 0.25 M pyrrole: (a) 0.1 M NaOH, (b) 0.01 M NaOH. Figures indicate the cycle numbers.

Electroactivity of the PPy was investigated by cyclic voltammetry in the two aqueous electrolytes. Figures 1(a) and 1(b) show the cyclic voltammograms in the electrolyte of 0.1 M and 0.01 M NaOH, respectively, scanned at 10 mV s^{-1} over the range between 0.0 V and 1.8 V vs. Ag/AgCl. At the first cycle, irreversible anodic currents are observed in both (a) and (b), and simultaneously PPy thin films are deposited on the ITO electrode. On the other hand, the polymerization current decreases sharply(a) or scarcely flows(b) after the first cycle. This means that the PPy films deposited from the NaOH basic solutions are electroinactive and nonconducting. It was reported by Li et al.[8)] that OH^--doping and undoping of an electroactive PPy are observed by cyclic voltammetry in a NaOH solution with a decrease in the conductivity of the PPy, but that OH^- ion reacts irreversibly upon the PPy chain at the high potential electrolysis. Judging from the inactivity of the PPy films in our experiment, it was supposed that the irreversible reaction occurs between the PPy or pyrrole monomer and OH^-. The reaction might take place between α or β-carbons and OH^- and form C=O groups in the polymer chain leading to the shortening of the π-conjugation length, which is similar to the overoxidation suggested by F. Beck et al.[9)]. The shape of the voltammogram (a) in the 0.1 M solution has another large peak at the first cycle, in contrast to (b) in the 0.01 M solution. The anodic peak at more positive potential in the voltammogram (a) is related to an oxygen evolution current judging from the results of blank solution. In the blank solution without pyrrole monomer, the current for the oxygen evolution was distinctly detected at more than 0.90 V in the similar voltammogram of both NaOH concentrations. Therefore, the PPy film from the 0.01 M NaOH solution is suggested to be more tight, and the morphology of the PPy is probably influenced by the OH^- concentration. From scanning electron microscopy(SEM) observations, the PPy film from the 0.1 M solution became rougher and thicker film compared with that from the 0.01 M solution. Accordingly, we selected the 0.01 M NaOH solution for preparing the insulation layer of the MIM device.

The electropolymerization of the PPy for the MIM device was operated by potentiostatic electrolysis, which prepared the same inactive PPy film at 1.5 V vs. Ag/AgCl. The PPy film in the 0.01 M NaOH solution was ascertained by the SEM graphs to be thin and smooth, and the MIM device using the PPy film gave reproducible I-V characteristics. Figure 2 shows the relation between current and voltage for the MIM device using the PPy film electropolymerized for 50 min. The positive and negative directions in Fig. 2(a) and 2(b) correspond to positive and negative bias to the ITO electrode, respectively. It can be seen in Fig. 2(a) that the current behavior is symmetrical for positive and negative voltage, and the increase of non-linear current becomes nearly 5 orders between 0.5 V and 10 V. The device shows the possibility of practical use for switching by the threshold sharpness at ±5 V in Fig. 2(b).

Since the initially deposited PPy film was insulated state, the current flow for electrolysis and the growth of film ceased immediately after the start of potentiostatic control. No appreciable change of the film thickness(ca. 0.2 μm) was actually observed between the films electrolyzed for 15 min and 60 min by SEM or a talysurf measurement. However, the

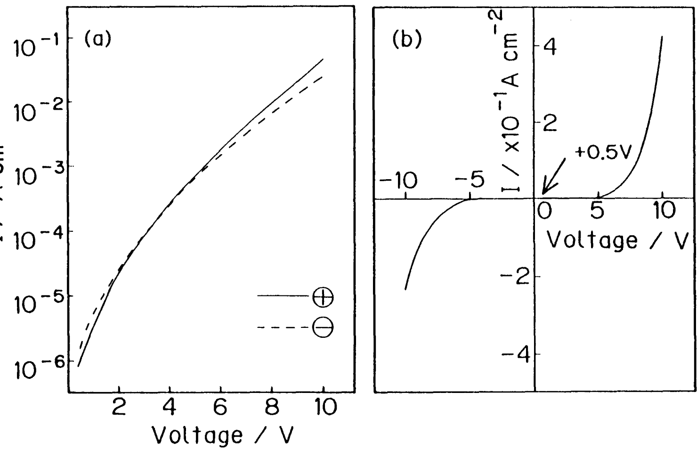

Fig. 2. I-V characteristics of an ITO/PPy/ITO device. PPy was electropolymerized for 50 min: (a) logI-V, (b) I-V.

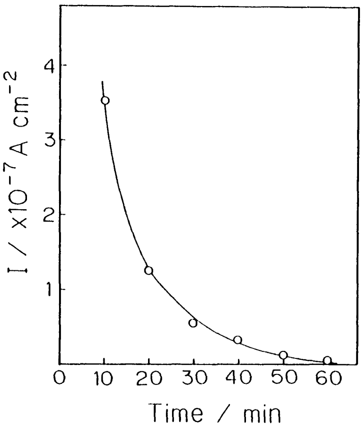

Fig. 3. Currents through the devices at the voltage of +0.5 V as a function of electrolyzed time.

currents at the bias voltage of 0.5 V in the I-V curves clearly change as a function of the electrolyzed time, i. e., the insulation resistance of the PPy increases with electrolyzed time. The currents at 0.5 V(see an arrow position in Fig. 2 (b)) are shown in Fig. 3. The increase in the insulation resistance may imply the decrease in pin-hole condition of the film, which is supported by the results that the MIM devices using the PPy films polymerized less than 20 min easily become breakdown at the high electric field of 10 V. Thus, the satisfactorily tight and pinhole-free PPy film is considered to be formed with sufficient electrolysis time irrespective of no growth of film thickness.

In conclusion, the electroinactive and nonconducting PPy film electropolymerized in the NaOH solution was proved to be an excellent insulator for the MIM device. It can be used as-prepared condition, which is more desirable for the application to the MIM device than the previously reported one.[4)] Moreover, the MIM device using the PPy deposited from the NaOH solution is also superior to the previous one with respect to the stability of I-V characteristics.

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