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Electrochemical Synthesis of Polypyrrole Films Containing Metal Oxide Particles

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Electrochemical oxidation of pyrrole has been undertaken in aqueous suspensions of metal oxides in the presence and absence of hydroxides. It has been found that polypyrrole films containing oxide particles can be prepared for oxides having the isoelectric point smaller than pH ca. 4.5 provided that pH of the oxide suspensions is high enough to build up negative charges on the oxide surfaces.

It is well-established that in the preparation of electroconductive polymers such as polypyrrole and polythiophene electrolyte anions are incorporated in the polymer films to compensate positive charges induced in polymer chains. By using the anion incorporation properties, special functions such as electrocatalytic activities[1-3)] have successfully been attached to polypyrrole (PPy) films. However, no report has been published concerning the incorporation of electrically neutral substances such as metal oxide particles. In this communication, the first achievement of the oxide incorporation, which may open a new route to functionalization of electroconductive polymers, will be described.

Pyrrole was dissolved in water to give its concentration of 0.1 mol dm^{-3}, and one of oxides listed in Table 1 was suspended in 50 cm^3 of the pyrrole solution. As shown in the table, the specific surface area of the oxides used were different, so the actual surface area of the oxide in the suspensions were different, but this does not bring about any serious errors in experimental results, as will be shown later in this paper. An one compartment cell was used as an electrolytic cell, and an Au plate of 1 cm^2 was used as the electrode substrate for the polymer deposition. The electrolysis was undertaken in quiet suspensions at 1 mA cm^{-2} at 25 °C without using a reference electrode to avoid any contanination from electrolyte solutions of the reference electrode. The amount of electrolysis charges chosen was 900 mC cm^{-2}. The achievement of the oxide incorporation was confirmed by electron probe X-ray microanalysis. Before this was done, the deposited polymers were rinsed with water, followed by washing with ethanol in an ultrasonic bath and then finally dried in air. It is thought that for the oxide incorporation to occur oxide surfaces should negatively be charged, and such conditions are achieved when pH of the suspensions is greater than the isoelectric point of oxides. Since the quantity of negative charges on oxide surfaces becomes

Table 1. Results Obtained by Electrolysis of Pyrrole in Oxide Suspensions

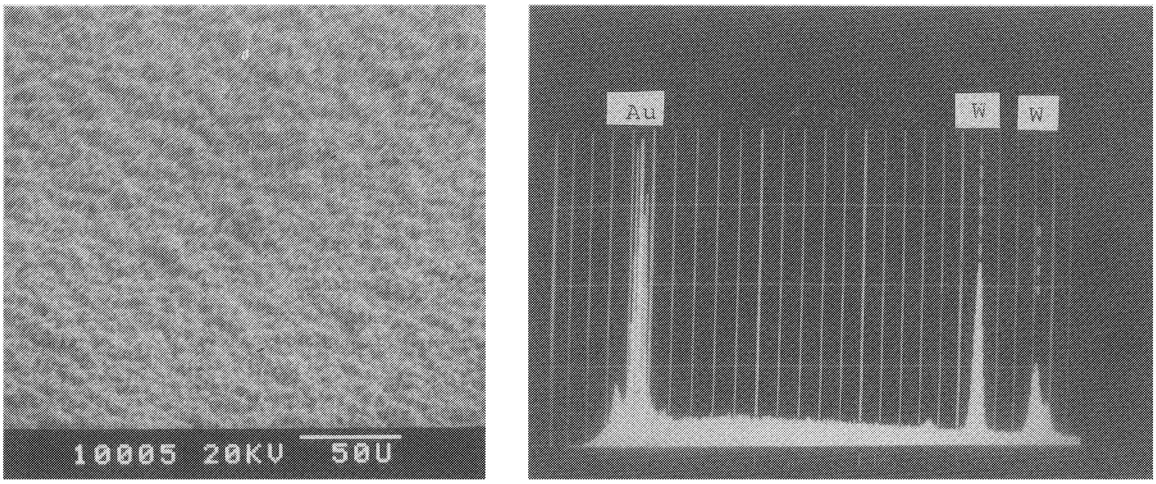
Oxide	Sp. Area (m^2g^{-1})	iep[a] (pH)	Amount suspended (g/50 cm^3)	pH of suspension (pH)	Oxide incorporation	Morphology of PPy
WO_3	1.04	0.54[4]	0.10	5.0	Yes	thick film
			1.53	4.8	Yes	thick film
SiO_2	1.45	1.8[4]	1.11	7.6	Yes	thick film
			0.10	5.9	Yes	thick film
Ta_2O_5	3.27	2.9[4]	0.49	7.5	Yes	thin film
			0.10	6.5	Yes	thin film
			0.49	10.0[b]	Yes	thin film
SnO_2	28.6	4.5[4]	0.056	6.0	Yes	thin film
			0.056	8.2	Yes	thin film
TiO_2	160	6.0-6.7[4]	0.01	7.1	No	very thin deposit
			0.01	8.0[b]	No	very thin deposit
	16.9		0.10	7.0	No	very thin deposit
CeO_2	11.7	6.8[4]	0.137	10.0[b]	No	very thin deposit
MnO_2	25.9	7.3[5]	0.10	8.0[b]	No	very thin deposit
			0.066	10.0[b]	No	very thin deposit
ZnO	9.55	9.0[4]	0.167	10.0[b]	No	very thin deposit

a) Isoelectric point.

b) Appropriate amount of 0.1 mol dm^{-3} NaOH was added to make pH values indicated.

large with increasing pH of suspensions from the isoelectric point of the oxide, several suspensions were made alkaline by adding an appropriate amount of a NaOH solution. However, it was needed to set upper limits for pH of the suspensions; it was found in oxide-free pyrrole solutions containing conventional electrolytes such as NaCl and Na_2SO_4 that the PPy deposition does not occur if polymerization bathes have pH >11.

In Table 1, electrolysis results are given together with isoelectric point data of oxides and pH of oxide suspensions used for electrolysis. Among metal oxides investigated, WO_3 and SiO_2 were successfully incorporated in PPy films during the course of polymer film deposition, and dense and thick PPy films were produced seemingly in proportion to electrolysis charges. Figure 1 shows a picture of PPy film surfaces containing WO_3, taken by a scanning electron microscope, together with an X-ray spectrum taken simultaneously. The PPy film produced looked as if WO_3 had covered the entire surfaces. Almost the same was true for the SiO_2 incorporation. PPy films containing incorporated Ta_2O_5 and SnO_2 also could be prepared, but in these cases PPy films produced were very thin, and the film growth did not seem to occur with increasing electrolysis charges. In cases of using the other oxides the oxide incorporation did not occur, and the Au electrode was covered with a very thin deposits of polymers which did not form a uniform film. During the course of electrolysis, a fraction of the suspended oxides fell to the bottom of the electrolysis cell, the tendency being



(a) (b)

Fig. 1. Picture of PPy film surface containing WO_3(a) and X-ray spectrum of the surface (b).

greater for oxides having smaller specific surface area. Nevertheless, the oxide incorporation markedly took place for WO_3 and SiO_2 which had the smallest specific surface area. Then the judgement is made that the surface area does not play an important role in the oxide incorporation.

According to the results given in Table 1, the isoelectric point of oxides seems to play an important role in deposition behaviors of PPy; the smaller the the isoelectric point, the thicker the resulting polymer films. This finding is closely related to results obtained on activities of the resulting PPy films for redox reactions of $Fe(CN)_6^{4-/3-}$. According to cyclic voltammograms shown in Fig. 2, the magnitude of redox waves was different among PPy films containing different oxides. A couple of redox waves appeared at PPy film electrodes prepared in oxide-free 0.1 mol dm^{-3} pyrrole containing 0.1 mol dm^{-3} NaCl. Almost the same magnitude of the redox waves appeared at a PPy electrode containing WO_3, though capacitive currents were bigger at this electrode than at the oxide-free PPy electrode. A PPy electrode containing SiO_2 gave a little small and broad redox waves (not shown). In contrast, redox waves at a PPy electrode containing Ta_2O_5 were very small, and the shape of voltammograms seems to be resulted from resistive nature of the PPy film. The same was true for a PPy electrode containing SnO_2. It is recognized from these results that the isoelectric point of oxides controls the conductivities of resulting PPy films. Similar findings have already been reported for electrolyte anion incorporations, where the smaller the dissociation constant of conjugated acids of electrolyte anions, the greater the conductivities of PPy films produced.7) The effect of the dissociation constant observed can reasonably be explained in terms of electrostatic interaction between negative charges of anions incorporated in PPy films and positive charges (polarons/and or bipolarons) induced in polymer chains; greater interaction results in smaller conductivities, and such situations are expected for PPy films containing more basic anions. In the case of the oxide incorporation, a quite similar situation seems to hold. Oxides

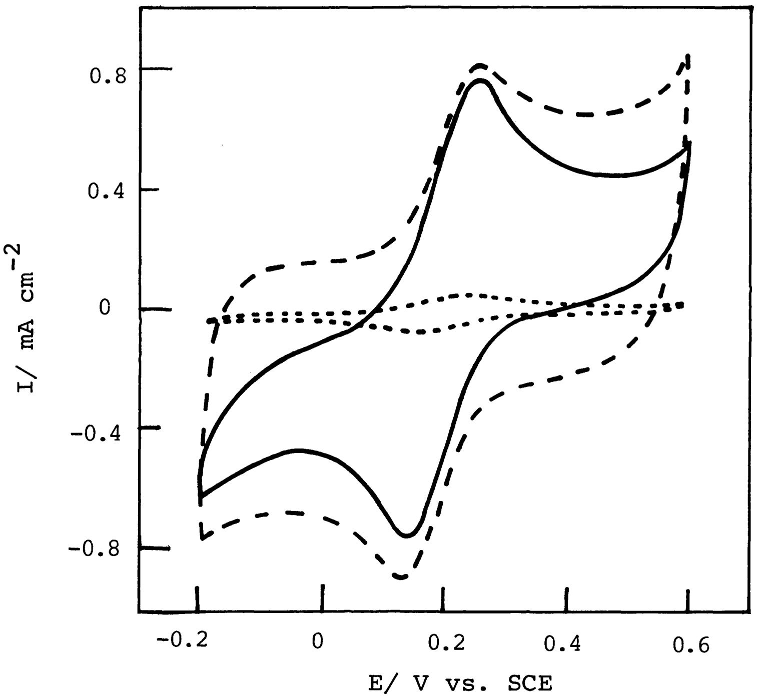


Fig. 2. Cyclic voltammograms of 5×10^{-3} mol dm^{-3} $K_3Fe(CN)_6$ in 0.1 mol dm^{-3} Na_2SO_4 at 50 mV s^{-1}. (——) PPy containing Cl^-, (— —) PPy containing WO_3, and (·····) PPy containing Ta_2O_5.

having large isoelectric point possess high affinities to positively charged protons, and then when they are incorporated in PPy, they interact strongly with positive charges of polymer chains, resulting in resistive PPy films. Such differences in the conductivity seem to influence greatly growth behaviors of PPy films. In cases where the deposition of highly resistive PPy occurs, anodic polarization at 1 mA cm^{-2} raises the electrode potentials to such positive values as to cause decomposition of PPy, and then the growth of PPy films does not appreciably occur. Anyway, the present study has shown in the first time that it is possible to incorporate electrically neutral substances in PPy films, though there is some limitations, and the principle discovered here must have great utilities in practical applications of PPy.

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References

1) K. Okabayashi, O. Ikeda, and H. Tamura, J. Chem. Soc., Chem. Commun., 1983, 684.
2) R. A. Bull, F. R. Fan, and A. J. Bard, J. Electrochem. Soc., 131, 687 (1984).
3) J. S. Foss, and S. M. Erker, J. Electrochem. Soc., 133, 1983 (1986).
4) G. A. Parks, Chem. Rev., 65, 177 (1965).
5) M. A. Butler and D. S. Ginley, J. Electrochem. Soc., 125, 238 (1978).
6) T. W. Healeey, A. P. Henning, and D. W. Fuerstenau, J. Colloid Interf. Sci., 21, 435 (1966).
7) S. Kuwabata, J. Nakamura, and H. Yoneyama, J. Chem. Soc., Chem. Commun., 1988, 779.

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