

Characteristics and Sensing Behavior of Electrochemically Codeposited Polypyrrole–Poly(vinyl alcohol) Thin Film Exposed to Ethanol Vapors

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ABSTRACT: Polypyrrole–poly(vinyl alcohol) (PPy–PVA) composite films were prepared electrochemically by means of codeposition at a constant potential. Their sensing behaviors to various ethanol-vapor concentrations were investigated. Increasing the molar fraction of PVA up to PPy_{0.964}PVA_{0.036} showed an increase of the sensitivity of the composite sensors. However, the sensitivity decreased if further PVA was incorporated. The ethanol-sensing behaviors were also largely dependent upon the electropolymerization charge, ranging from 50 to 200 mC in this investigation. Higher sensitivity was measured from the composite film prepared with a lower electrical charge. For example, a sensitivity of 7.70 mΩ mg⁻¹ L, about 3.3 times the sensitivity of the pristine PPy sensor, was measured by the PPy_{0.964}PVA_{0.036} composite film prepared at 50 mC. However, incorporating PVA into the conducting polymer was at the sacrifice of the response speed as well as the stability of the composite as it was under continuous exposure to ethanol vapor. An adsorption model based on the Langmuir isotherm was used to interpret the sensing behaviors and the equation derived from this model correlated well with the measured sensitivities. The sensing parameters including the adsorption equilibrium constant, K_m , and the resistance change caused by a pseudomonolayer, $[m(r_1 - r_2)]/n$, were determined and found to decrease with increasing polymerization charge. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 73: 2079–2087, 1999

Key words: PPy; PVA; composite film; electrochemical codeposition; ethanol vapor

INTRODUCTION

Early work on conducting polymers as gas sensors was undertaken by a number of groups and the first disclosure of the gas-sensing properties of conducting polymers was made by Nylander et al. in 1983.¹ They used polypyrrole (PPy)-impregnated filter paper to measure the response to ammonia vapor. Later, the same device was used to

measure the responses to NO₂ and H₂S under suitable conditions; presumably, these gases reacted with PPy by oxidizing and reducing the Ppy, respectively. Bartlett's group^{2–4} compared the responses to vapors such as alcohols, acetone, and ether from four different polymers including PPy, polyaniline, poly-*N*-methylpyrrole, and poly-5-carboxyindole. It was reported that poly-5-carboxyindole gave the most consistent response to all the vapors investigated and the mechanism of the response of these sensors was explained in terms of semiconductor theory.⁴

Among these organic conductive polymers, PPy is one which has frequently been studied as a gas sensor^{1,3} due to its excellent properties of stability

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and flexibility. Bruschi et al.⁵ proposed a method based on the chemical polymerization of pyrrole vapor onto a pattern with metal chlorine salt as an oxidizing agent. Bartlett et al.⁴ proposed a method using electrochemical deposition of conducting polymers in the development of a gas sensor. The major problem with PPy is its very fragile nature. To improve the characteristics of the films, some authors proposed to blend the conducting polymer with some stabilizing materials. Several PPy-based composites, such as PPy-PVC,⁶ PPy-polyamide,⁷ PPy-polyester,⁸ PPy-PTFE,⁹ and PPy-poly(ethylene oxide) (PEO) [10] as gas sensors had been studied.

Ojio and Miyata¹¹ blended PPy and poly(vinyl alcohol) (PVA) by gas-state polymerization for obtaining transparent and conducting polymers. Lindsey and Street¹² studied the PPy-PVA composite films prepared by electrochemical polymerization onto a pre-coated PVA matrix. These studies concluded that PPy-PVA composite films combine the advantageous mechanical properties of the host polymer with the electrical properties of PPy. It should be a worthwhile subject to modify the brittle PPy with PVA for improving its gas-sensing properties as well as its stability. However, it was also pointed out¹³ that the initial deposition of PPy occurred mainly at the pre-coated insulating matrix-electrode interface and led to surface, rather to bulk, conduction of the composite film. It was also observed that the conductivities on the electrode side were generally more reproducible than on the solution side of the composite films, where PPy was inhomogeneously deposited. Therefore, we adopted a new approach to prepare a composite film through the electrochemical codeposition of a conductive polymer and the insulating polymer to prevent their inhomogeneous distribution. In our previous work,¹⁴ we reported that a great improvement in sensitivity to methanol vapors was achieved by a PPy-PVA composite film prepared by an electrochemical codeposition process. In this article, we present not only the results of a further study on the behaviors of such a composite exposed to ethanol vapor prepared by the same method but also the validity of the proposed adsorption model as it is applied to interpret the experimental results.

EXPERIMENTAL

An interdigitated gold electrode screen-printed onto the surface of an alumina substrate was

used. Its structure and dimensions were same as that in our earlier report.¹⁴ The electrode was first deposited with a very thin layer of PPy by a method of chemical oxidation described elsewhere.³ Chemiresistors were fabricated by the electrical deposition of these electrodes with the PPy-PVA thin film. PVA (DP = 500, Aldrich), completely dissolved in CH₃CN, was added into the cell for polymerization which contains 0.1M LiClO₄ (99%, Jassen) and 0.1M pyrrole monomers (99%, Janssen) under a N₂ atmosphere. Cyclic voltammetry measurements were carried out in a 0.1M LiClO₄ electrolyte system to determine the polymerization potential. Using a platinum reference electrode, PPy and PVA were codeposited onto the electrode surface at a constant potential of 0.75 V versus SCE with various electrical charges ranging from 0.05 to 0.20 C. The deposited polymer layers were then washed with CH₃CN several times and dried in an oven at 90°C for 5 h. The responses of the sensor, which was properly positioned in a glass reactor, to the ethanol vapor, premixed with N₂ gas in a glass bead-filled chamber and introduced into the reactor, were measured by a device consisting mainly of an I-V meter and a data acquisition system. The response time and recovery time were obtained by measuring the time to reach 95% of the plateau value. The film morphology was investigated by scanning electron microscopy (Cambridge Stereoscan S360). The molar fractions of PVA in the composite films were determined by an elemental analyzer (Perkin-Elmer 2400).

RESULTS AND DISCUSSION

Electropolymerization of PPy-PVA Composite

A cyclic voltammography was carried out at 100 mV/s to determine the potential for the growth of pyrrole on the electrode in an aqueous LiClO₄ solution. It reveals that the current density rises above 0.5 V versus SCE due to the oxidation reaction of the pyrrole monomer. However, an over-oxidation effect would occur on the PPy if the potential applied was set too high. Accordingly, the electropolymerization was carried out at 0.75 V versus SCE. Measurements were then undertaken at room temperature and after the current had stabilized. The linearity of the current versus voltage was obtained and this characteristic confirmed that the ohmic contacts had been established between the gold electrode and the poly-

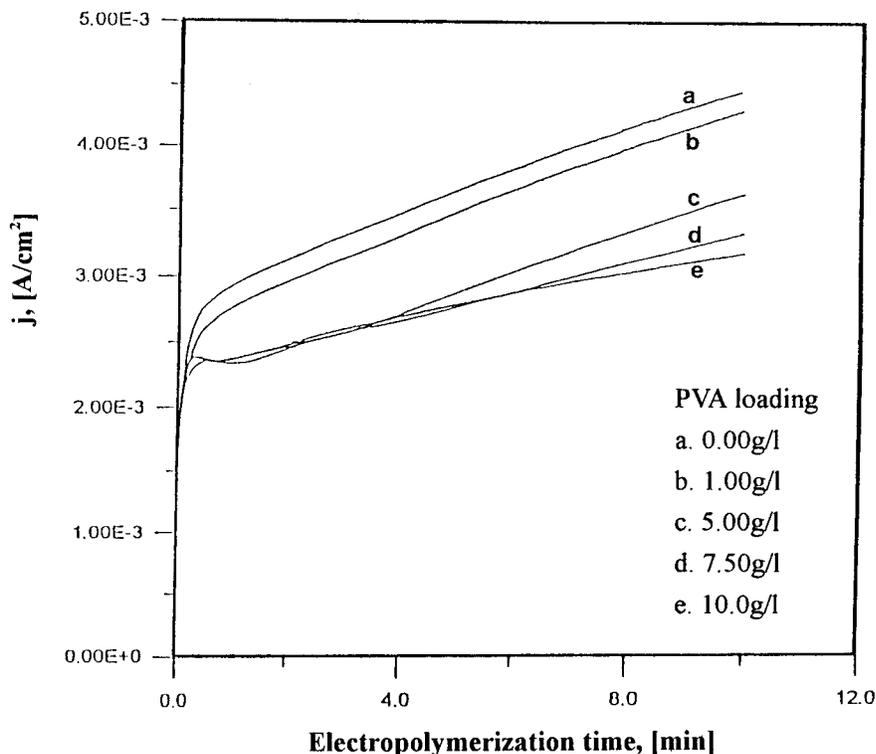


Figure 1 Current density versus polymerization time at 0.75 V (versus SCE) for various loadings of PVA in a 1M pyrrole + 0.1M LiClO₄ solution.

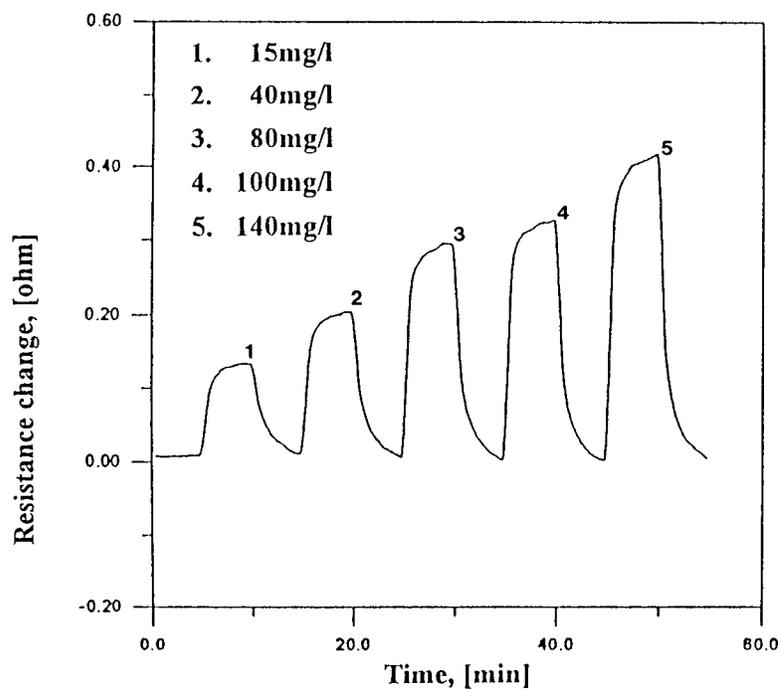
mer. PPy and PVA were codeposited on a stainless-steel electrode by adding a proper amount of PVA into the electrolytic solution. The current density plotted against the polymerization time with various PVA loadings is shown in Figure 1. With a constant voltage of 0.75 V, the current density increased instantly up to a transition current and then increased steadily with increase of the polymerization time. The higher loading of PVA in the solution, the lower the transition current density that resulted. This may be attributed to the less active sites for the nucleation of PPy on the hydrophilic surface of the electrode. The instant increase of the current density was due to the deposition of the first monolayer of PPy. However, all would reach a transition current density quickly. The decrease of the transition current density with increase of the PVA loading in the electrolytic solution was attributed to the higher resistance due to the addition of the insulating PVA.

Effect of Ethanol Vapor Concentration

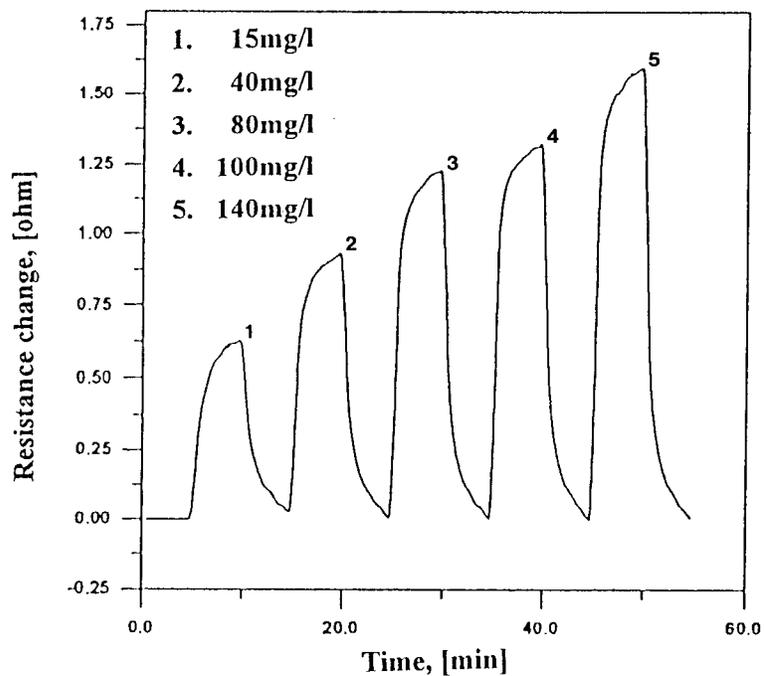
The responses of the pure PPy, electropolymerized with 50 mC, to the ethanol vapor carried by

nitrogen gas are shown in Figure 2(a), in which the resistances were plotted against time with five cycles of different concentrations of ethanol exposure. It is well known that PPy is a P-type semiconductor. Therefore, the exposure of electron-donating gases such as alcohol to PPy causes a decrease in conductance. As can be seen, the resistance change increases with increasing the ethanol concentration from 15 to 140 mg/L. The responses of the PPy-PVA composite exposed to various concentrations of ethanol vapors are shown in Figure 2(b), in which, similar to pristine PPy, the resistance is shown to be increasing with the ethanol vapor concentration and the reproducibility is good.

Figure 3(a,b) shows the resistance changes of PPy and PPy_{0.964}PVA_{0.036}, where the subscripts stand for the respective molar fractions of PPy and PVA, plotted against the ethanol concentrations, respectively. It shows that the resistance changes for both are linearly proportional to the ethanol concentration and the slope of the linearity was specified as the sensitivity of the polymer sensor, that is, the resistance change (ΔR) per unit ethanol vapor concentration. The sensitivity

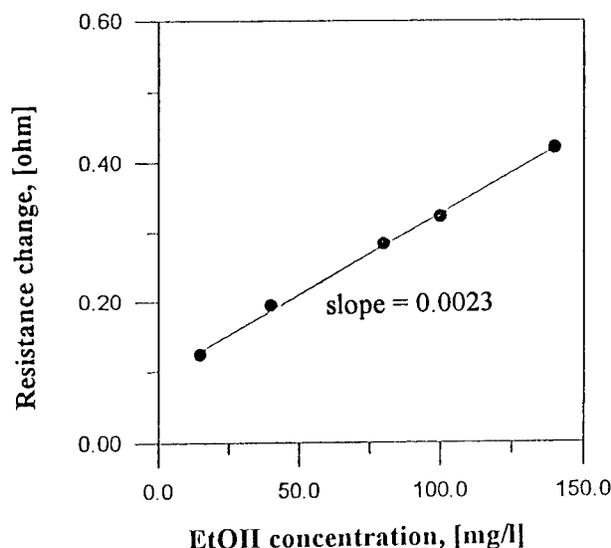


(a)

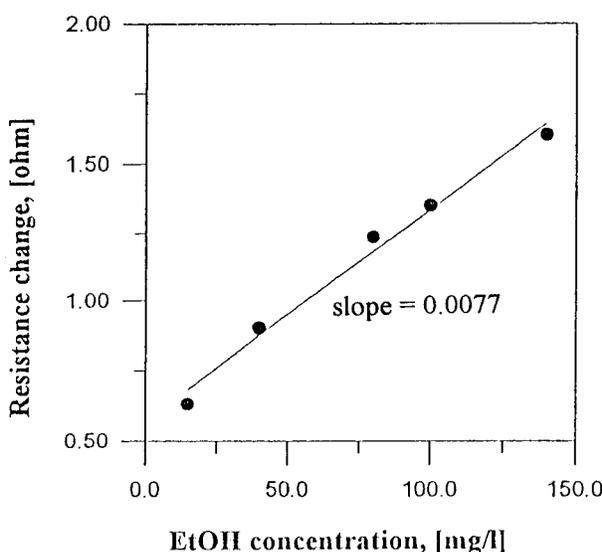


(b)

Figure 2 Responses of (a) PPy and (b) PPy_{0.964}PVA_{0.036} to ethanol vapor in various concentrations.



(a)



(b)

Figure 3 Resistance changes of (a) PPy and (b) PPy_{0.964}PVA_{0.036} plotted against ethanol concentrations.

of the pure PPy sensor to the ethanol vapor was thus 2.32 mΩ mg⁻¹ L if polymerized at 50 mC. Similarly, the sensitivity of PPy_{0.964}PVA_{0.036} was also obtained by the same method and was measured to be 7.70 mΩ mg⁻¹ L, which is about 3.3 times the sensitivity of the pristine PPy.

A comparison of the response times for pristine PPy and composite PPy_{0.964}PVA_{0.036} are tabulated in Table I. As can be seen, the response time for the PPy_{0.964}PVA_{0.036} was 196 s for the ethanol concentration at 15 mg/L and 142 s at 140 mg/L. On the other hand, the response time for the pristine PPy was 94 and 130 s when the ethanol concentration was 15 and 140 mg/L, respectively. Obviously, the PPy_{0.964}PVA_{0.036} took a longer time to respond to the ethanol vapor as compared with the PPy. The discrepancy became greater in the lower ethanol concentrations. The recovery time required for the PPy and PPy_{0.964}PVA_{0.036} to recover 95% of its original resistance from the shut-off of the ethanol vapor is also tabulated in the same table for comparison. As can be seen, the PPy_{0.964}PVA_{0.036} composite took 244 s to recover from an ethanol concentration of 15 mg/L and took 170 s from that of 140 mg/L. On the other hand, the pure PPy sensor exposed to the ethanol concentration of 15 mg/L took 186 s to recover, and exposed to a concentration of 140 mg/L, 208 s to recover. Accordingly, the incorporation of PVA made both the response time and the recovery time become longer.

These results were reversed to those obtained from the same composite sensors in ammonia gas,¹⁵ which led to a much quicker response and recovery actions. On the other hand, similar behaviors of response speeds and recovery speeds were obtained by the PPy-PVA composites exposed to methanol vapors.¹³ It may be attributed to that the adsorbed ethanol or methanol molecules bounded more tightly with hydrophilic groups on PVA and resulted in a slower adsorption and desorption rates. Generally speaking, PPy-PVA responds to the ethanol vapor more quickly in a higher concentration. However, the pristine PPy responded more quickly in a lower concentration than in a higher one. Meanwhile, it was also found that the forward response time is always shorter than is the recovery time.

Effect of Molar Fraction of PVA on the Sensitivity

In our previous work,¹⁰ on the PPy-PEO composite film prepared by the electrochemical codeposition process, we found that the molar fraction of PPy decreased as PEO loading in the electrolytic solution increased. Figure 4 shows the dependence of the molar fraction of PVA in the composite on the PVA loading in the electrolytic solution. Similar to the PPy-PEO composite, it was found that the molar fraction of PVA increased as the PVA loading in

Table I Comparison of Response Times and Recovery Times Required for PPy and PPy-PVA Sensors Exposed to Ethanol Vapors

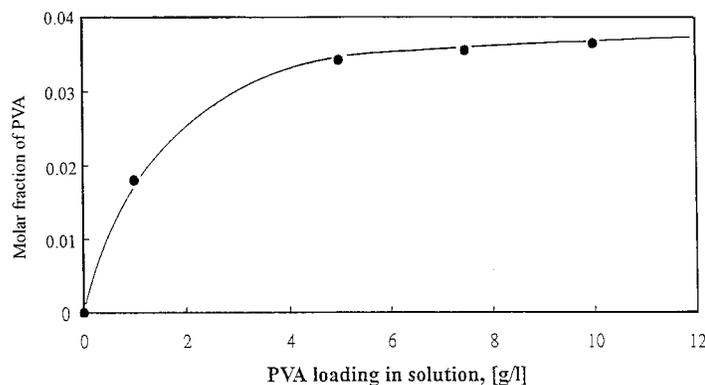
Ethanol Concentration (mg/L)	Response Time (s)		Recovery Time (s)	
	PPy	PPy-PVA	PPy	PPy-PVA
15	94	196	186	244
40	104	166	230	216
80	128	164	200	210
100	104	144	198	202
140	130	142	208	170

the solution increased, up to 7.5 g/L, and was kept nearly constant if a further amount of PVA was added into the electrolytic solution. The dependence of the sensor's sensitivity on the molar fraction of PVA was investigated and was found to have an order of $\text{PPy}_{0.964}\text{PVA}_{0.036}$ ($7.70 \text{ m}\Omega \text{ mg}^{-1} \text{ L}$) $>$ $\text{PPy}_{0.981}\text{PVA}_{0.019}$ ($4.35 \text{ m}\Omega \text{ mg}^{-1} \text{ L}$) $>$ PPy ($2.32 \text{ m}\Omega \text{ mg}^{-1} \text{ L}$). The reason why the higher PVA fraction in the composite resulted in higher sensitivity may be attributed to the higher porosity in the composite film, which led to a higher surface area for adsorption. As PVC was added into the electrolytic solution and the macromolecules were brought onto the electrode surface together with the formation of PPy, it was reasonable to expect that the PVA phase would result in a much coarser morphology of the composite film than would the pure PPy phase, which is true if we compare the scanning electron microscopies shown in Figure 5(a-c). As can be seen, the apparent surface roughness of the films have an order of $\text{PPy}_{0.964}\text{PVA}_{0.036}$ $>$ $\text{PPy}_{0.981}\text{PVA}_{0.019}$ $>$ PPy. We concluded that the incorporation of PVA would result in a different morphology and lead to a porous structure. It is well

known that higher porosity usually leads to a better response due to a higher diffusion rate and higher gas adsorption but at the expense of its selectivity. However, an excessive addition of PVA may shield the active sites of the electrode and result in a morphology that may be too coarse to form a continuous phase and decrease the sensing performance. We concluded that a proper amount of PVA, approximately 7.5 g/L, would result in a $\text{PPy}_{0.964}\text{PVA}_{0.036}$ composite and would be able to increase greatly the sensitivity of the PPy-based sensors to ethanol vapor.

Stability of the Composite Sensor Exposed to Ethanol Vapor

A comparison of the sensitivity decay for the $\text{PPy}_{0.964}\text{PVA}_{0.036}$ and PPy sensors is illustrated in Figure 6. As can be seen, both PPy and $\text{PPy}_{0.964}\text{PVA}_{0.036}$ in this study exhibited decreasing stability as they were undergoing a continuous aging in the ethanol environment. However, the sensitivity of the $\text{PPy}_{0.964}\text{PVA}_{0.036}$ composite decays more readily than does the pure PPy. In

**Figure 4** Relationship of the molar fraction of PVA in the composite film on the PVA loading in the electrolytic solution.

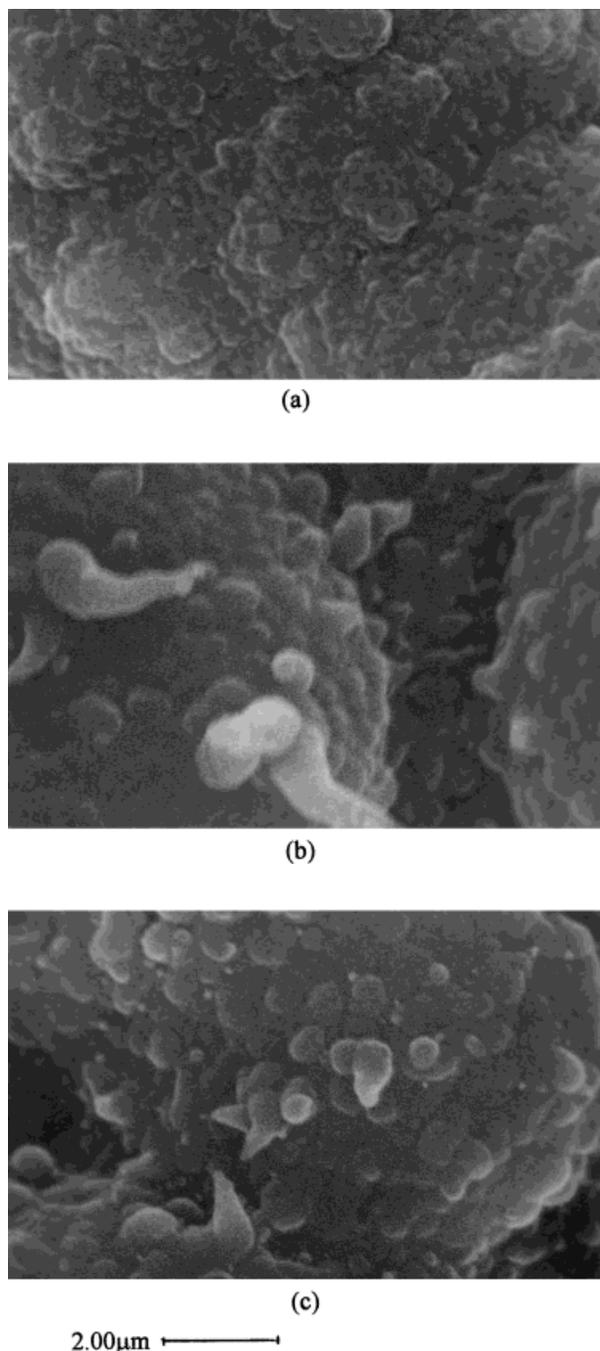


Figure 5 Scanning electron microscopies of (a) pure PPy, (b) $\text{PPy}_{0.981}\text{PVA}_{0.019}$, and (c) $\text{PPy}_{0.964}\text{PVA}_{0.036}$.

other words, the incorporation of PVA in the PPy conductive matrix reduced the stability of the sensor material. A similar result was found by the same composite sensor exposed to methanol vapor in our previous work,¹³ which was ascribed to the hydrophilic nature of PVA that was more easily affected by moisture and tightly bounded with

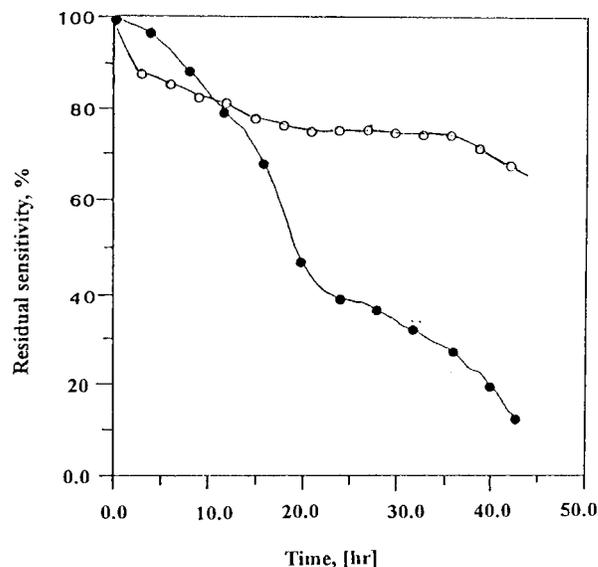


Figure 6 Sensitivity decays of (○) PPy and (●) $\text{PPy}_{0.964}\text{PVA}_{0.036}$ thin films exposed to ethanol vapor.

ethanol vapor. However, an improved stability in the PPy-PVA composite sensor was found as it was exposed to ammonia and these results will be published elsewhere soon.¹⁵ Therefore, we suggest that PPy-PVA composite sensors are more suitable to detect nonalcohol gases due to the stability concern.

Effect of Polymerization Charge

The effects of polymerization charges upon the sensitivities of the PPy-PVA composite films are shown in Figure 7. It can be seen that the sensitivity decreased with increase of the polymerization charge. Certainly, these differences in the

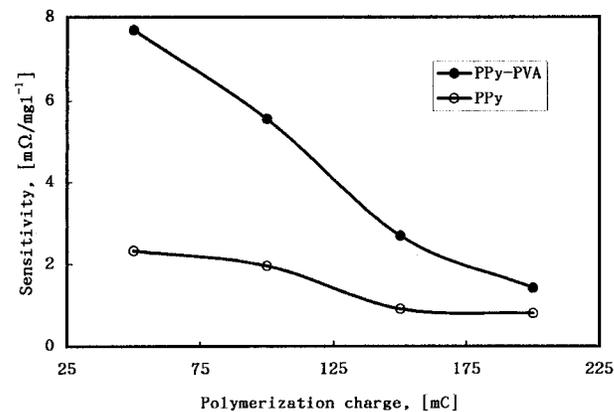


Figure 7 Dependence of sensitivity on the polymerization charge.

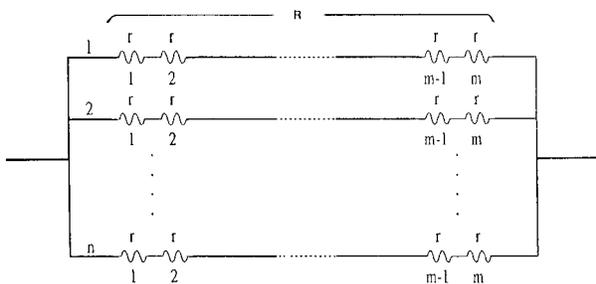


Figure 8 A microscopic model for a composite sensor prepared by an electrochemical codeposition process.

sensitivities are mainly induced by the variations in the thickness, the morphological structure, as well as the molar fraction of PVA in the composite film. A thicker polymer film would be formed if higher electrical charges were applied. In other words, the magnitude of the resistance change was higher if the composite film was thinner. We have to remind the reader that the magnitude of the electropolymerization charge may also have an effect on the morphological structure of the composite film and, consequently, leads to a different sensing performance.

We had proposed a microscopic gas-sensing model previously,¹⁰ based on the Langmuir isotherm, to explain the behaviors of PPy-PEO sensors to methanol vapors. The overall resistance of the composite film can be regarded as the paralleling of several layers of the resistor and each layer is composed of several resistors in series, as shown in Figure 8. In this figure, R , r , n , and m represent the resistance of a pseudomonolayer, the resistance of an active site, the thickness of the sensing film, as well as a number of active sites on a monolayer, respectively. The plot of the reciprocal of the resistance change against the reciprocal of the gas concentration is a linear relationship according to the following equation based on the proposed model¹⁰:

$$\frac{1}{\Delta R_t} = n/[m(r_1 - r_0)] + \{n/[m(r_1 - r_0)K_m]\}(1/C_{A0})$$

where ΔR_t is the resistance difference after and before gas sorption; K_m , the adsorption equilibrium constant; C_{A0} , the concentration of the detected gas; and r_1 and r_0 , the site resistances as the site is vacant and occupied, respectively. This

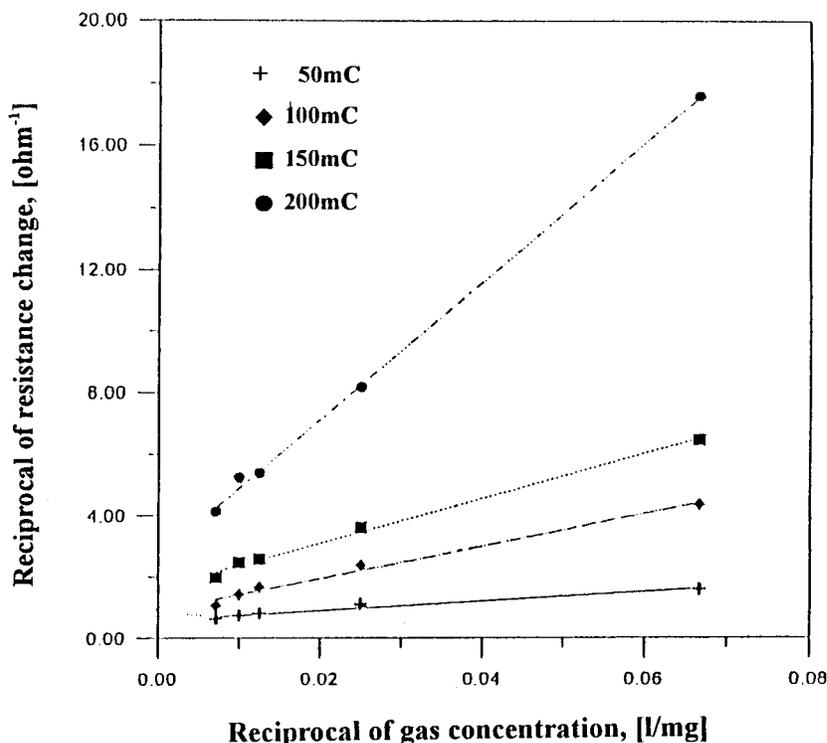


Figure 9 Reciprocal of resistance change plotted against reciprocal of gas concentration for PPy-PVA thin films prepared with various polymerization charges.

Table II Parameters of $[m(r_1 - r_0)/n$ and K_m Based on the Microscopic Sorption Model and Figure 9

	50 mC	100 mC	150 mC	200 mC
$m(r_1 - r_0)/n$	1.661	1.120	0.605	0.375
K_m	0.039	0.017	0.023	0.012

equation indicates the dependence of the sensitivity of the gas sensor on the active-site number of a monolayer, the thickness of the polymer film, the adsorption equilibrium constant, and the change of the site resistance. Figure 9 shows such a relationship through plotting $1/R_t$ against $1/C_{A0}$ and the linear relationship proves that the experimental results correlate very well with the proposed model. The parameters of $n/[m(r_1 - r_0)]$ and K_m can be obtained from the determinations of the intercept and the slope of the plot. It was reported¹⁰ that this model interpreted well the behaviors of PPy-PEO composite sensors exposed to ethanol vapor by comparing the experimental results. As can be seen from Table II, the values of $(m/n)(r_1 - r_0)$ and K_m decrease with increasing electrical charge. Actually, K_m is dependent upon the affinity of the sensing material and manifested itself as a smaller value as the film became thicker. Accordingly, a lower sensitivity would have resulted if a higher polymerization charge was applied.

CONCLUSIONS

Incorporation of a proper amount of PVA (e.g., PPy_{0.964}PVA_{0.036}) could improve the sensitivity of PPy-based sensors to ethanol vapor up to 3.3 times. However, incorporation of PVA in the composite sensor lowered both the response and recovery speeds to ethanol vapor as compared with the pristine PPy. The sensitivity of the composite sensor was greatly dependent upon the electrical polymerization charge and exhibited a higher sensitivity if a lower electrical charge was applied. Incorporation of PVA also reduced the stability of the sensor as it was continuously exposed to ethanol vapors. A proposed sorption model

based on the Langmuir isotherm was used to interpret the sensing behaviors of the composite sensors and the experimental results of the sensitivity correlated well with the sensing equation based on this model. A linear relationship of $1/\Delta R_t$ plotted against $1/C_{A0}$ was obtained and the parameters, $(m/n)(r_1 - r_0)$ and K_m , determined from this plot were found to decrease with the polymerization charge. It was hinted that a thin polymeric composite film with high affinity would be a promising direction to develop a better sensing material.

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