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Gas Sensitivities of Polypyrrole Films to Electron Acceptor Gases

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Electropolymerized polypyrrole films exhibited noticeable gas sensitivities to electron acceptor gases such as PCl_3, SO_2, and NO_2 at room temperature only when they were reduced electrochemically, and the resistance decrease was larger with the gas of larger electron affinity. It was also found that the resistance decrease obeyed the Elovich equation in an early stage of the gas exposure.

Conducting polymers such as polypyrrole and polyaniline have a characteristic feature that anion-doping reactions occur reversibly, and this property has been utilized in several applications such as rechargeable batteries,[1-3] electrochromic displays[4-6] and electronic devices.[7,8] The use of conducting polymers as gas-sensing elements has also been reported in the case of polypyrrole for ammonia,[9] nitrogen dioxide,[10] and alcohols.[11] We previously investigated[12] the NO_2 sensing mechanism of polypyrrole films and found that the NO_2 sensitivity was mainly indebted to chemical doping of NO_2 to give NO_2^-, as in the case of polyacetylene with iodine and bromine etc.[13,14] and of polypyrrole with iodine vapor.[15,16] The present study was intended to investigate comparatively the gas sensitivity of polypyrrole to several electron acceptor gases such as O_2, PCl_3, SO_2, NO_2, and I_2.

Experimental

Film Preparation. Electropolymerization of pyrrole was performed in acetonitrile containing 1 vol% twice distilled water, 0.1 mol dm^{-3} $LiClO_4$ and 0.1 mol dm^{-3} pyrrole under N_2 atmosphere. Distilled pyrrole, reagent grade $LiClO_4$, and acetonitrile were used for the preparation of the electrolyte solution, and prior to electrolysis N_2 was bubbled into the solution for more than 20 min to purge dissolved oxygen. An electrode used for gas sensitivity measurements is illustrated in Fig. 1. Two pieces of Pt wires (d=0.5 mm) were connected to a Pyrex male ground glass joint with 0.3 mm distance which was provided by inserting a thin adhesive tape between the Pt electrodes. The separation of the Pt electrode was fixed with epoxy resin in such a manner as to leave 3 mm bare portion of the Pt wires in their ends which served as electrodes. The polypyrrole deposition was made with the electrolysis at 1 mA for 20 min. By the electrolysis, polypyrrole was deposited in such a manner as to connect the two Pt wire electrodes with each other.

The preparation of polypyrrole films for elemental analyses and for EPMA was made using a rectangular ITO glass electrode (4.0×1.5 cm^2) and a circular ITO glass electrode with 10 mm diameter, respectively. The electrolysis was carried out at 0.5 mA cm^{-2} for 30 min for both cases.

Polypyrrole films used for an multireflectance FT-IR measurement were prepared on a Pt-sputtered rectangular ITO glass electrode (4.0×1.5 cm^2) which provided a flat reflective surface, and those for optical absorption spectrometry were prepared on a rectangular ITO glass electrode (2.5×1.5 cm^2) covered with a very thin Pt layer which assisted in homogeneous reduction of the deposited polypyrrole film. The covered Pt was thin enough to allow light penetration in the absorption measurements. In both cases, the current density of 0.2 mA cm^{-2} was used and the quantities of electricity chosen for the former and the latter were 200 mC cm^{-2} and 100 mC cm^{-2}, respectively.

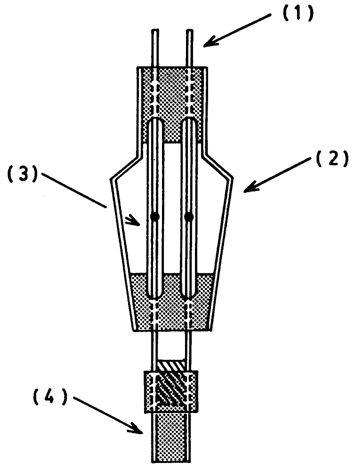

Fig. 1. Schematic illustrations of electrode used for the polypyrrole electrodeposition, designed for the gas sensitivity measurement. Dotted part and slash-lined part denote epoxy resin and adhesive tape, respectively.
(1) Cu lead wire, (2) ground pyrex glass male joint, (3) glass tube, (4) Pt wire (d=0.5 mm).

After thoroughly rinsed with acetonitrile, the electropolymerized polypyrrole films were transferred into a N_2-saturated dry box, and subjected to electrochemical reduction in distilled acetonitrile containing 0.1 mol dm^{-3} $LiClO_4$ at −400 mV (vs. Ag/AgCl) for longer than 15 min. Immediately after the reduction, the polypyrrole films were rinsed with distilled acetonitrile and then transferred into a vacuum vessel having a ground female joint which allowed the connection to a vacuum line. These procedures were conducted in the dry box. The polypyrrole samples were vacuum dried at ca. 10^{-4} Torr (1 Torr=133.322 Pa) for more than 1 h.

Measurements of Gas Sensitivities. The electrode shown in Fig. 1 was connected to a branch of a three way tubing. The branch contained a stopcock and a fitted female joint for connecting the electrode. Another branch of the tubing contained a stopcock through which a gas reservoir was connected. The gas reservoir contained an injection port like that of a gas chromatograph for the injection of test gases. The third branch of the tubing was connected to a vacuum line. Before measurements, the electrode housing and the gas reservoir were evacuated, stopcocks of them were then closed, and the test gas was introduced into the gas reservoir using a gas syringe so as to give 300 Pa in the whole cell. In the measurements of gas sensitivity to iodine vapor, however, solid iodine was first placed in the gas reservoir which was cooled by liquid N_2, and then the electrode housing and the gas reservoir were evacuated. The iodine vapor of ca. 27 Pa in the whole cell was prepared by warming the gas reservoir to room temperature. By opening the stopcock of the electrode housing part, the electrode was exposed to the test gas. Gas sensing behaviors of the polypyrrole films were obtained by measuring current transients under application of 100 mV. In this paper, the gas sensing behaviors will be shown by resistance-time relations. Oxygen, PCl_3, SO_2, NO_2, and iodine vapor which have electron affinities of 0.45 eV, 0.8 eV, 1.1 eV, between 2.1 and 2.5 eV and between 2.5 and 2.6 eV, respectively[17] were used as sample gases.

Spectral Measurements. Polypyrrole films were vacuum dried in the vessel connected to the vacuum line as in the case of the gas sensitivity measurements, and then exposed to sample gases for more than 1 h. After the vacuum evacuation of the gas-exposed films for more than 1 h, spectral measurements were carried out.

Electron probe X-ray microanalysis (EPMA) was performed using an energy dispersive X-ray analyzer EMAX-1800E (Horiba) connected to a scanning electron microscope S-450 (Hitachi). A FT-IR spectrometer FT/IR-3 (JASCO) and an UV-visible spectrometer MPS-5000 (Shimadzu) were used for multireflectance FT-IR measurements and the optical absorption measurements, respectively. The latter two measurements were performed in air.

Results and Discussion

Gas Sensitivities of Reduced Polypyrrole Films to Electron Acceptor Gases. The resistance of the polypyrrole films prepared in the electrode assembly shown in Fig. 1 was ca. 10 Ω and it increased to several kiloohms by electrochemical reduction. When the reduced polypyrrole films were exposed to either one of PCl_3, SO_2, or NO_2 in 300 Pa, or ca. 27 Pa I_2 vapors at room temperature, the resistance of the films was decreased as shown in Fig. 2, and the decreased resistance was not recovered by the subsequent vacuum evacuation. The O_2 sensitivity was also examined, but the exposure of the reduced polypyrrole film to 300 Pa O_2 did not result in any remarkable resistance change. This observation might be related to the finding reported by Scott et al. that the O_2 exposure of reduced polypyrrole films resulted in the conductivity of 10^{-2} S cm^{-1} at most,[18] the conductivity being the same order as that of reduced polypyrrole films used in this study.

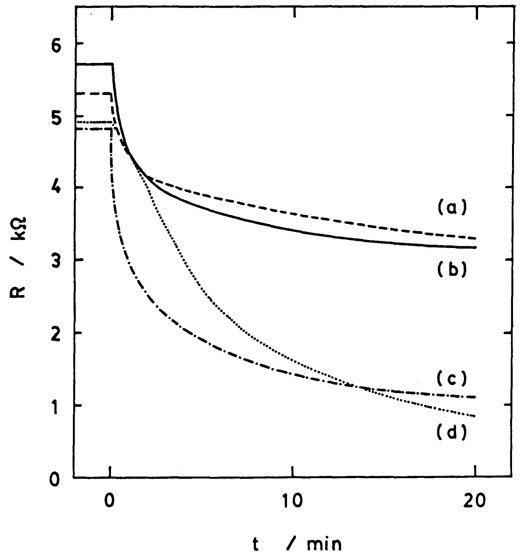

Fig. 2. Resistance changes of electrochemically reduced polypyrrole films caused by the exposure to electron acceptor gases:
(a) 300 Pa PCl_3, (b) 300 Pa SO_2, (c) 300 Pa NO_2, (d) ca. 27 Pa iodine vapor at room temperature.

It is shown in Fig. 2 that the initial resistance of reduced polypyrrole films were different. The scatter seems to have resulted from rather ill-reproducible connections of two Pt wire electrodes with the deposited polypyrrole, but it is believed that the difference in the initial resistances did not bring about any serious problem in qualitative analysis of the gas sensitivities of polypyrrole films which will be described below. It is seen in Fig. 2 that the gas sensitivities to iodine and NO_2 are larger than those to SO_2 and PCl_3. This was true even for the gas exposure for long term such as for more than 10 h. The resistance decrease rapidly occurred within initial ca. 2 hours of the gas exposure, followed by a gentle decrease. The resistance attained at the 10 h-gas exposure was 10^2 Ω for the iodine vapor, 1.8×10^2 Ω for NO_2, 1.8×10^3 Ω for SO_2 and 2.0×10^3 Ω for PCl_3. Considering that the electron affinity of NO_2 and I_2 is very near to each other and is more than 1 eV greater than those of PCl_3 and SO_2, the electron affinity seems to play an important role in determining the gas sensitivity of polypyrrole films.

Gas-Sensing Mechanisms. To analyze the resistance changes as shown in Fig. 2, FT-IR and optical absorption spectra of reduced polypyrrole films were measured before and after the gas exposure. Spectra of the reduced film, that of a film first reduced and then exposed to the sample gases, and that of an as-grown film are shown in Fig. 3. The reduced film gave a spectrum (a), while the as-grown film (b). Spectra (c), (d), and (e) concern polypyrrole films that were first reduced and then exposed to NO_2, SO_2, and PCl_3, respectively. It is shown for all cases that by the gas exposure the absorption around 1 eV was enhanced, while that around 3 eV was decreased. It is well-established that absorption having its maximum around 1 eV is related to bipolaron-related transition which is dominant in anion-doped polypyrrole, and that around 3 eV is related to π-π* transition which is

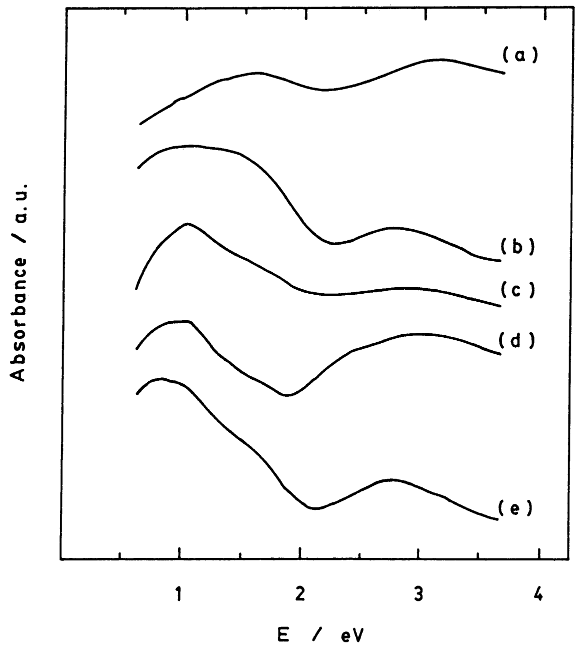

Fig. 3. Optical absorption spectra of polypyrrole films:
(a) reduced, (b) as-grown, (c) reduced and then exposed to NO_2, (d) reduced and then exposed to SO_2, (e) reduced and then exposed to PCl_3.

Table 1. Elemental Analyses of Various Polypyrrole Films[a]

Sample	Molar ratio to carbon (C=4)				
	C	H	N	Cl	I
As-grown	4	3.03	0.96	0.33	—
Reduced	4	2.83	0.97	0.11	—
Reduced and then exposed to iodine vapor	4	3.20	1.00	0.11[b]	0.36[c]
Reduced and then exposed to NO_2	4	3.03	1.11	0.08	—
Reduced and then exposed to PCl_3	4	3.78	0.95	0.33	—

a) The exposure to each gas was carried out for 12 h at room temperature. The gas pressure was 300 Pa for NO_2 and PCl_3, and ca. 27 Pa for iodine vapor. b) Based on the results obtained for the reduced film. c) Estimated by subtracting the chlorine content from the total halogen content (see text).

dominant in reduced polypyrrole.[18,19] Then it is concluded that the resistance change of polypyrrole films caused by the exposures to SO_2 and PCl_3 results from the doping reactions, as already reported for iodine[15,16] and NO_2[12] exposures.

Figure 4 shows FT-IR spectra for reduced films before and after SO_2-exposure. It is recognized that new absorption peaks appeared at 493, 634, 930, 940, 976, and 987 cm^{-1} with the SO_2-exposure. If polypyrrole reacts with SO_2 to give sulfur compounds like sulfone, sulfate and sulfonate, absorption should appear between 1100—1400 cm^{-1},[21] being in contradiction to the obtained results. It is known that SO_2 gives absorption peaks at 1147, 517, and 1351 cm^{-1},[21] SO_2^- at 984.8, 495.6, and 1042 cm^{-1},[21] SO_3 at 484, 1391, and 536 cm^{-1},[21] SO_2^{2-} at 967, 620, 933, and 469 cm^{-1},[21] and SO_4^{2-} at 981 and 1104 cm^{-1}.[21] Judging from these published data, new peaks which appeared in the spectrum (b) are attributable to doped SO_2^- and SO_3^{2-}. Multireflectance FT-IR spectrum of reduced and then PCl_3-exposed polypyrrole film was also measured. The spectrum showed the absorption around 500 cm^{-1} which is related to P–Cl stretching. However, due to lacking of published absorption data of compounds containing P and Cl, the identification of the doped anion species has not yet been done.

Table 1 shows results obtained by elemental analyses of as-grown films, reduced films, and films reduced and then exposed to one of the sample gases used. The data are given as the relative molar ratio of each elements to carbon which is fixed to 4, the number being equal to that of carbon atoms of a pyrrole ring. It was found that the reduced polypyrrole films contained 0.11 moles of ClO_4^- per unit mole of pyrrole probably due to difficulty of complete undoping in a thick film used for elemental analysis. Since the elemental analysis of halogens gives information not on each kind of halogen but on the sum of all kinds of halogens included in the polypyrrole film, the amount of iodine of iodine-exposed polypyrrole films was deduced by subtracting the amount of chlorine content of the reduced polypyrrole films from the total halogen content determined. The sulfur content could not be determined, because the analysis is unsuccessful in the presence of both chalcogen and halogen.

By counting the difference in nitrogen content between the reduced film and the reduced and then NO_2-exposed one, the amount of nitrogen species doped by the NO_2-exposure is deduced to be 0.14 atoms per pyrrole ring. The doped nitrogen species must be NO_2^-.[12] In the case of iodine-exposed film, the amount of doped anionic species would be 0.12 per pyrrole ring, because it is highly probable that the doped iodine species is I_3^-.[20] When the reduced polypyrrole film was exposed to PCl_3, chlorine was increased by 0.22 atoms per pyrrole ring. Though the doped anionic species produced by the PCl_3-exposure has not yet been known, the number of doped anions would be 0.07 per pyrrole ring if a single ionization to give PCl_3^- is assumed to take place on the doping. The finding that the doped ionic species was smaller in the PCl_3-doped film than in the iodine-doped films and NO_2-doped one correlates well with the resistance decrease caused by the gas exposure (Fig. 2). It is then concluded that the degree of anion doping caused by the gas exposure is primarily controlled by the electron affinity of the exposed gas.

Chemisorption Kinetics of Exposed Gases. It was found that the resistance changing behavior as shown in Fig. 2 follows to the Elovich equation (Eq. 1), which is applicable to slow kinetics of chemisorption under a constant gas pressure,[22]

$$\frac{\mathrm{d}v}{\mathrm{d}t} = a \exp(-bv) \qquad (1)$$

where v is the amount of an adsorbed species, a and b represent the rate of adsorption at $v=0$ and the relative rate of disappearance of active sites for chemisorption, respectively. Integration of Eq. 1 gives Eq. 2.

$$v = \frac{1}{b}\ln\left(t + \frac{1}{ab}\right) + \frac{1}{b}\ln(ab) \qquad (2)$$

It is thought that the conductivity of gas-exposed polypyrrole film is proportional not to the amount of adsorbed gas but to the amount of ionized dopants. Then the v of the Elovich equation should be read to be the amount of ionized dopant. Since it is believed that the anion doping in polypyrrole occurs like adsorption on polymer fibrils, the establishment of the Elovich equation in the doping process is not strange provided that the ionization is rate-determining in the gas sensing. It is of significance to remark here that the resistance change was observed only when components of the exposed gases were detected in the polypyrrole films.

If it is assumed that the film conductance is proportional to the amount of doped anionic species,[23] then Eq. 3 holds,

$$\frac{1}{R} = Kv \qquad (3)$$

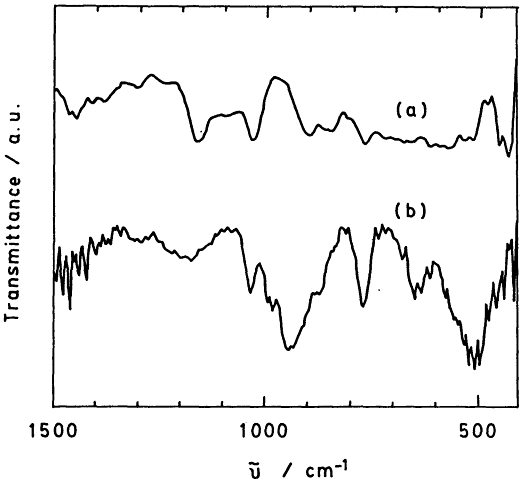

Fig. 4. Multireflectance FT-IR spectra of polypyrrole films:
(a) reduced, (b) reduced and then exposed to SO_2.

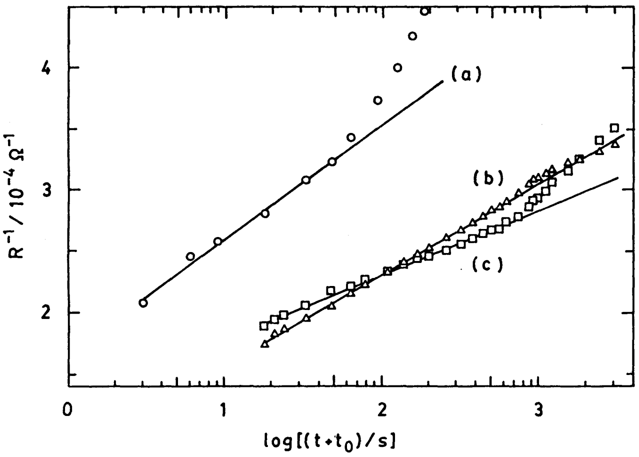

Fig. 5. Elovich plots of the resistance changes shown in Fig. 2.
(a) 300 Pa NO_2, (b) 300 Pa SO_2, (c) 300 Pa PCl_3.

Table 2. Parameters Related to the Adsorption of Electron Acceptor Gases in Polypyrrole films

	E_a[a)]	K/b	t_0	Ka
	eV	$s^2 A^2 m^{-2} kg^{-1}$	S	$s A^2 m^{-2} kg^{-1}$
NO_2	2.1<, <2.5	4.06×10^{-5}	3	1.35×10^{-5}
SO_2	1.1	3.19×10^{-5}	18	1.77×10^{-6}
PCl_3	0.8	2.29×10^{-5}	18	1.27×10^{-6}

a) Electron affinity.

where R is the resistance of polypyrrole films and K is a proportional constant. It seems important to remark here that Eq. 3 is not always valid; electrostatic interaction between dopants and positive charges induced in polypyrrole may sometimes greatly influence the conductivity.[24] However, the assumption of Eq. 3 seems to be valid as long as the results obtained at least for NO_2, SO_2, and PCl_3-exposure, as will be shown below. By combining Eq. 3 with Eq. 2, Eq. 4 is derived,

$$\frac{1}{R} = \frac{K}{b}\ln(t+t_0) - \frac{K}{b}\ln(t_0) \qquad (4)$$

where t_0 is an adjustable variable to establish a linear relation between $1/R$ and logarithms of the gas exposure time and satisfies $t_0=1/ab$. The application of this equation to the time course of the resistance change shown in Fig. 2 gives Fig. 5 for NO_2, SO_2, and PCl_3 in an initial stage of the gas exposure, if t_0 values as given in Table 2 are used. In the case of the iodine vapor, however, the choice of any t_0 values failed to give a linear relation. In Table 2, K/b and Ka values which were determined from $t_0=1/ab$ and the slope of the linear relations are also given. The Ka gives a measure of the easiness of the ionization in an initial stage of gas exposure, because the a concerns the rate of adsorption at $v=0$, and K is the proportional constant in Eq. 3 which is believed to be eventually the same among the kind of gases used as long as this equation is valid. Then the results in Table 2 clearly shows that the gas having larger electron affinity has a higher tendency to be ionized.

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