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ORIGINAL PAPER

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Characteristics of Pd/Nafion electrodes prepared by an impregnation-reduction method in sensing hydrogen

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Abstract The influences of reductant concentration and Pd loading on the response and recovery times and the sensitivity in detecting hydrogen of Pd/Nafion electrodes prepared by an impregnation-reduction method were investigated in this study. The Pd/Nafion electrodes with a Pd loading of 6.90 mg/cm^2, obtained at 0.006 M $Pd(NH_3)_4Cl_2$ and 0.06 M $NaBH_4$, show the maximum sensitivity of 0.0519 μA/ppm in the H_2 concentration range 0–4410 ppm. However, the Pd/Nafion electrodes with a Pd loading of 11.42 mg/cm^2, obtained at 0.01 M $Pd(NH_3)_4Cl_2$ and 0.06 M $NaBH_4$, show the fastest response and recovery speed in sensing hydrogen. Generally, the response time decreases with an increase of the hydrogen concentration, but the recovery time increases with an increase of the hydrogen concentration. A sensing model is also proposed to illustrate the sensing phenomenon.

Key words Impregnation-reduction method · Palladium/Nafion · Sensitivity · Response and recovery times

Introduction

It is known that electrochemical gas sensors based on a solid polymer electrolyte (SPE) have the advantages of simplifying product separation and purification, diminishing side reactions, and permitting the construction of miniature devices [1, 2, 3]. Nafion, a copolymer of tetrafluoroethlyene and vinyl ether sulfonyl fluoride, is one of the most interesting SPEs for both scientific and technological research [4, 5, 6, 7]. Recently, much effort has been devoted to the development of sensing gases using the Nafion membrane as a SPE. Moreover, Nafion modified by means of metalization [8, 9, 10, 11, 12, 13], especially with noble metals, can produce composite materials with ionic and electronic conductivity characteristics which are very important in gas sensing. For catalytic purposes, metals can be deposited onto Nafion electrodes by chemical reduction processes [14, 15], which are divided into two different kinds: the Takenata-Torikai method (T-T method) [16, 17] and the impregnation-reduction method (I-R method) [18, 19]. Since a mechanically stable electrode with a high surface area can be obtained easily by a chemical reduction process [20], it has aroused great interest recently. Most studies in the literature [3, 17] are contributive just to the sensitivity behavior of the electrodes. However, the characteristics of spatial distribution and compactness of the deposited metal onto Nafion film can be revealed from the response and recovery times of the electrodes in sensing gases. The response and recovery times also demonstrate the kinetic performance of an electrode. Moreover, they are more important in actual practice.

This paper presents an amperometric detector for sensing hydrogen on a Nafion electrode modified with palladium coated on one side, prepared by an I-R method. The influences of reductant concentration and Pd loading on the response and recovery times and the sensitivity of the electrodes in detecting hydrogen were wholly examined, to obtain complete knowledge of the electrode's performance. The relationship between the characteristics of the Pd/Nafion electrode and the sensing performance was also investigated.

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Experimental

Pd deposition onto Nafion by the I-R method

A piece of 25 × 25 mm and 0.0432 mm thick Nafion 117 (DuPont, cation exchange type) was boiled in 3% H_2O_2 for 40 min and then rinsed with distilled water. The Nafion film was dipped in 9 M HCl at 80 °C for 50 min to exchange it for the H^+ type, rinsed again several times with distilled water, and then cleaned in an ultrasonic bath for 15 min. Afterwards the film was boiled in distilled water for 30 min to wash out the surplus H^+ and the pretreated film was stored in deionized water before use. The Pd layer was obtained by exposing only one side of the membrane to a 0.006 M $Pd(NH_3)_4Cl_2$ solution fixed at pH 11.5 for 3 h, followed by washing the impregnated membrane with distilled water and then exposing it again for another 2 h to an alkaline solution with $NaBH_4$ as the reductant. The experimental temperature was maintained at 35 °C with a water bath. The Pd loading was determined from the difference of the concentrations of $Pd(NH_3)_4^{2+}$ before and after depositing Pd onto the Nafion film, using an atomic adsorption spectrophotometer (AAS). Thus, various $Pd(NH_3)_4^{2+}$ concentrations of 0.002, 0.004, 0.006, 0.008, and 0.010 M, corresponding to a Pd loading of 2.31, 4.59, 6.90, 9.18, and 11.42 mg/cm^2, respectively, were obtained with 0.06 M $NaBH_4$. SEM and XRD were used to examine the morphology and crystal size of the Pd deposited onto the film, respectively.

Electrochemical characteristics

All electrochemical experiments were performed using a potentiostat (model 273A, EG&G) with a sensor geometric surface of 0.238 cm^2 at ambient temperature. Figure 1 shows the schematic diagram of the sensing cell structure. The electrochemical cell comprised two compartments. The Pd/Nafion composite behaved as a separator dividing the anode and cathode compartments. The anodic oxidation of hydrogen was carried out in the divided cells with Pd/Nafion as the working electrode, a Pt/Ti gauze as the counter electrode, and Ag/AgCl as the reference electrode. The anode and cathode chambers were filled with test gases and 1 M H_2SO_4, respectively. The various concentrations of hydrogen in the H_2-N_2 mixtures were prepared using a mass-flow-rate controller (model 840 Mass Meter) and were expressed by ppm (v/v) H_2. Polarization curves were obtained using a potentiostat, as already mentioned.

Results and discussion

Characteristics of the Pd/Nafion electrodes

From SEM observations and X-ray diffraction analysis, the results reported elsewhere [21] show that the particle size decreases and the Pd/Nafion electrodes become more compact with increasing reductant concentration, and the crystalline Pd with (111) orientation is found to be dominant and independent of the reductant concentration. Meanwhile, the average crystalline diameter decreases with an increase in the reductant concentration. The quantity of Pd loading increases with an increase of the reductant $NaBH_4$ concentration or an increase of the $Pd(NH_3)_4Cl_2$ concentration, as expected, but only the active surface area of the deposited Pd can actually determine the sensing performance of a Pd/Nafion electrode. The effects of the Pd loading and the $NaBH_4$ concentration on the active surface area are supposed to exist at an optimum condition for sensing gases, as in the Pt/Nafion system [22]. This indicates that the electrode will become too compact when the quantity of Pd loading or the $NaBH_4$ concentration exceeds the optimum. These are consistent with the observations of the SEM pictures [21]. These results are also consistent with the observation of the sensor's performance, which will be discussed later.

Current-potential relation

To estimate the exact sensing current for hydrogen, the current difference between the presence and absence of hydrogen was plotted against the potential, as shown in Fig. 2. The detected current rises to a plateau with the applied potential, being positive at more than 0.2 V vs. Ag/AgCl. This indicates that the hydrogen oxidation reaction is diffusion controlled at a more anodic

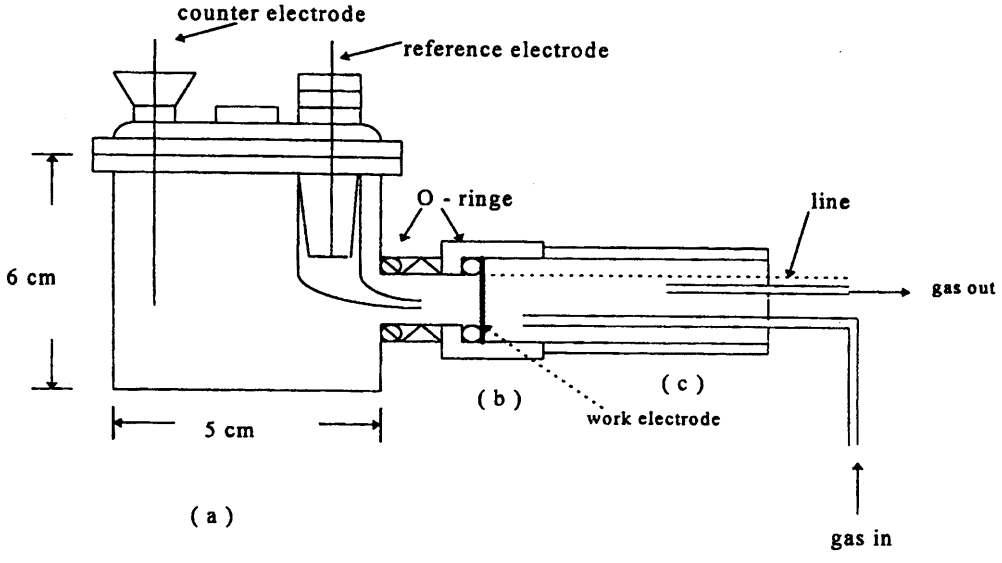

Fig. 1 Schematic diagram of the sensing cell structure: *a* reactor; *b* connector; *c* gas chamber

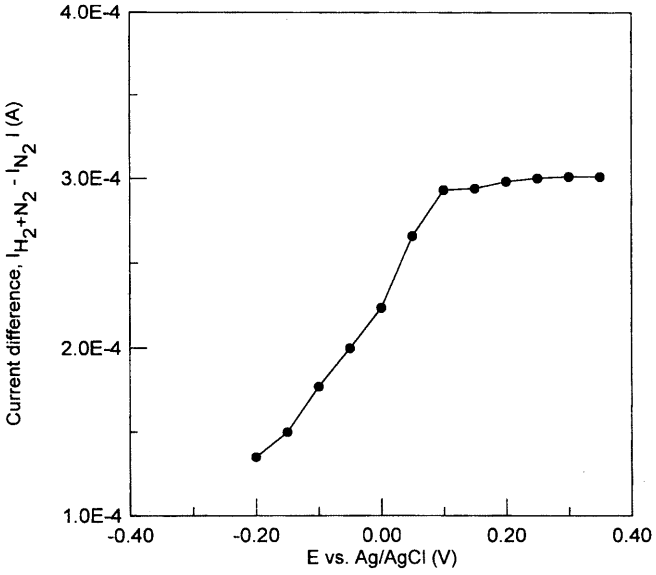

Fig. 2 Current difference in the presence of 2730 ppm H_2 and in the absence of H_2

potential than 0.2 V. Thus, all the sensing hydrogen experiments were performed by using a polarization potential of 0.2 V vs. Ag/AgCl in this work.

Linearity and sensitivity

The response current of the sensors can be controlled by the diffusion rate of bulk hydrogen in the gas boundary layer (r_1) and by the oxidation rate of hydrogen (r_2) at active sites within the Pd/Nafion layer, as indicated in Fig. 3. The reaction kinetics can be expressed by:

$$r_1 = k_m(C_b - C_s) \tag{1}$$

$$r_2 = k_s \eta C_s \tag{2}$$

where k_m and k_s are the mass transfer coefficient and the rate constant, respectively, η is the catalytic effectiveness factor, while C_b and C_s are the bulk H_2 concentration and the interfacial H_2 concentration between the gas and the Pd/Nafion layer, respectively. The catalytic effectiveness factor [23] can be expressed as:

$$\eta = (3/\Phi^2)(\Phi \coth \Phi - 1) \tag{3}$$

where the Thiele modulus (Φ) for a slab system can be expressed as:

$$\Phi = L(k_c S_a \eta_p / D_e)^{1/2} \tag{4}$$

where L, S_a, ρ_p, k_c, and D_e are the thickness of the Pd film, the internal surface area per unit mass of catalyst, the density of the catalyst, the intrinsic rate constant, and the effective diffusivity, respectively. The term $S_a\rho_p$ represents the surface area per unit volume of catalyst (A). Decreasing the particle size of the catalyst leads to an increase in this term. However, the effective diffusivity decreases when the electrode becomes more compact.

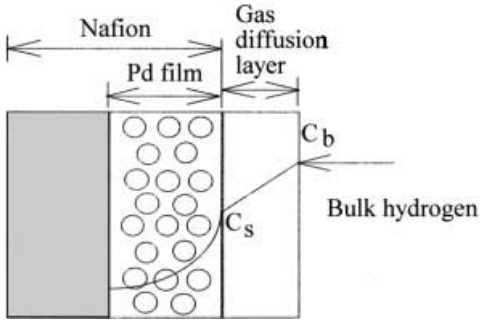

Fig. 3 Concentration profiles of hydrogen in the sensing system of a Pd/Nafion electrode

At a steady state, the response current of the sensor system can be derived from Eqs. 1 and 2 and be given as:

$$i = nFA \frac{1}{\frac{1}{k_m} + \frac{1}{k_s \eta}} C_b \tag{5}$$

Thus, a straight line can be obtained from the plot of sensing current, i, vs. bulk hydrogen concentration, C_b. The slope of the straight line represents the sensitivity (S), which can be expressed as:

$$S = \frac{nFA}{\frac{1}{k_m} + \frac{1}{k_s \eta}} \tag{6}$$

Since the sensing current is independent of the gas flow rate at a hydrogen concentration of 2585 ppm (data not shown here), it implies that the external diffusion resistance ($1/k_m$) can be neglected in this case and therefore Eq. 6 can be simplified as:

$$S = nFAk_s \tag{7}$$

Figure 4 demonstrates the response curves at various concentrations of hydrogen on Pd/Nafion electrodes prepared at 0.006 M $Pd(NH_3)_4Cl_2$ and different concentrations of $NaBH_4$. As shown in the response curves, increasing the concentration of H_2 leads to an increase in the sensing current. However, the sensing current increases and then decreases with increasing the concentration of $NaBH_4$. Figure 5 exhibits the detected steady currents of Pd/Nafion electrodes with different $NaBH_4$ concentrations at various H_2 concentrations. The slope of the straight line represents the sensitivity of Pd/Nafion electrodes in hydrogen sensing.

As shown in Fig. 5, the sensitivities increase with increasing the concentration of $NaBH_4$ up to a maximum value of 0.0519 μA/ppm at 0.06 M $NaBH_4$, and then decrease when the $NaBH_4$ concentration is over the optimum value. The higher sensitivity corresponds to a larger active surface area as expected. The results are consistent with the observation from the SEM and XRD experiments as mentioned before. The Pd particle

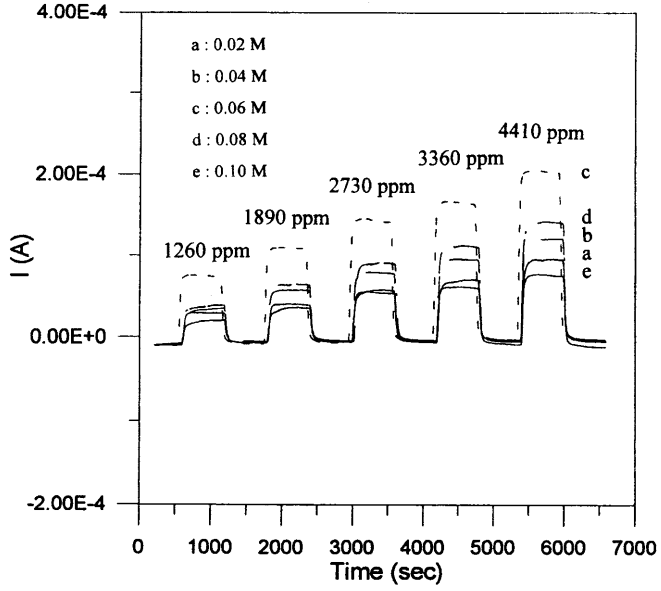

Fig. 4 Response curves for various concentrations of H_2 on a Pd/Nafion electrode with different concentrations of $NaBH_4$

size decreases and the Pd/Nafion electrodes become more compact with increasing the reductant concentration at a fixed quantity of Pd loading. This implies that a larger sensing active area results from a smaller individual particle size at a fixed Pd loading. However, the deposited Pd becomes a more compact and overlapping layer when the $NaBH_4$ concentration exceeds the optimum, which results in a lower active surface area. As shown in Fig. 5, the sensitivities increase significantly from 0.0227 to a maximum of 0.0519 μA/ppm with an increase in the $NaBH_4$ concentration from 0.02 to 0.06 M, but decrease suddenly with a further increase in the $NaBH_4$ concentration in the H_2 concentration range 0–4410 ppm.

Figure 6 shows the response curves at various concentrations of hydrogen on Pd/Nafion electrodes with different Pd loadings. As shown in the response curves, increasing the concentration of hydrogen leads to an increase in the sensing current. However, the sensing current increases and then decreases with increasing Pd loading. Figure 7 exhibits the detected steady currents of Pd/Nafion electrodes with different Pd loadings at various H_2 concentrations.

The sensitivities increase with an increasing quantity of Pd loading up to a maximum value and then decrease when the Pd loading is over the optimum value, as shown in Fig. 8. The reason for this can be explained from inspection of Eq. 6. The surface area of the Pd/Nafion electrodes (A) increases with an increase in Pd loading. The electrodes become more compact, therefore the effective diffusivity decreases when the Pd loading increases. From Eq. 4, increasing A ($S_a\rho_p$) and decreasing D_e with an increase in Pd loading lead to an increase in the Thiele modulus and consequently a decrease in the effectiveness factor η. Thus, the product of k_s and η has a maximum value with increasing Pd loading. Since the mass transfer coefficient k_m is negligible, the overall reaction is dominated by the internal diffusion resistance within the Pd/Nafion electrode. Therefore, the sensitivity is directly proportional to the value of $nFAk_s\eta$ as expected. As shown in Fig. 8, the sensitivities increase significantly from 0.00516 to a maximum of 0.0519 μA/ppm with an increase in Pd loading from 2.31 to 6.90 mg/cm^2, but decrease suddenly with a further increase in Pd loading in the H_2 concentration range 0–4410 ppm. The results are con-

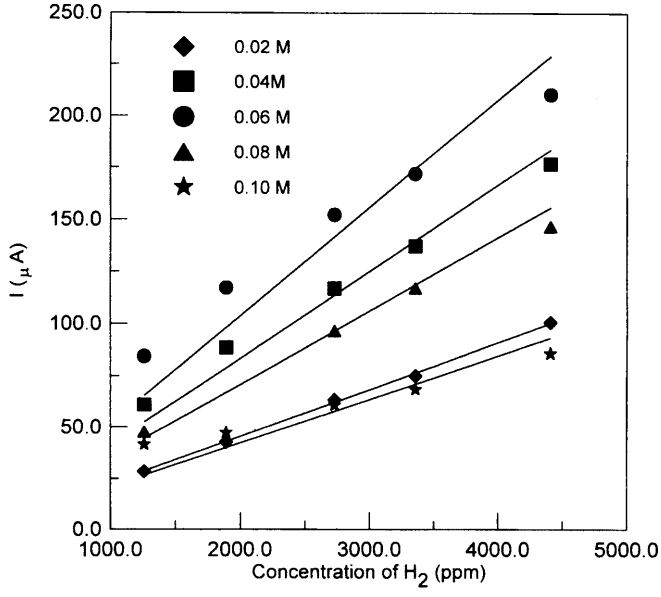

Fig. 5 Detected steady current of a Pd/Nafion electrode prepared at 0.06 M $Pd(NH_3)_4Cl_2$ as a function of the $NaBH_4$ concentration in 2730 ppm H_2

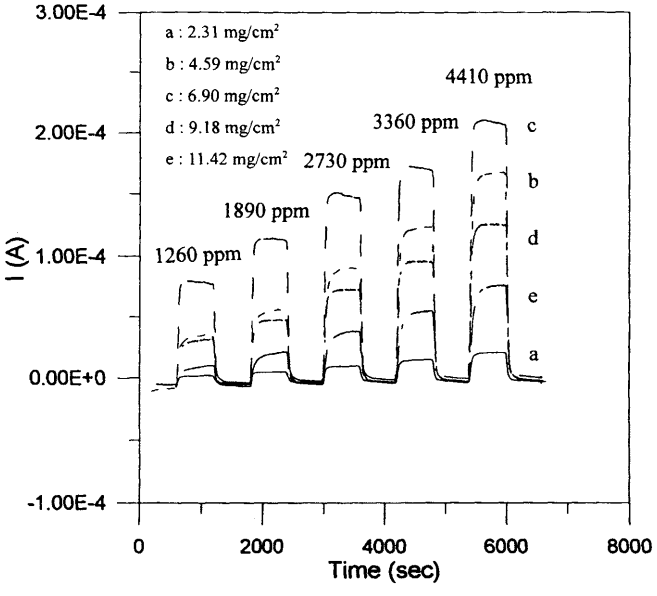

Fig. 6 Response curves for various concentrations of H_2 on a Pd/Nafion electrode with different Pd loadings

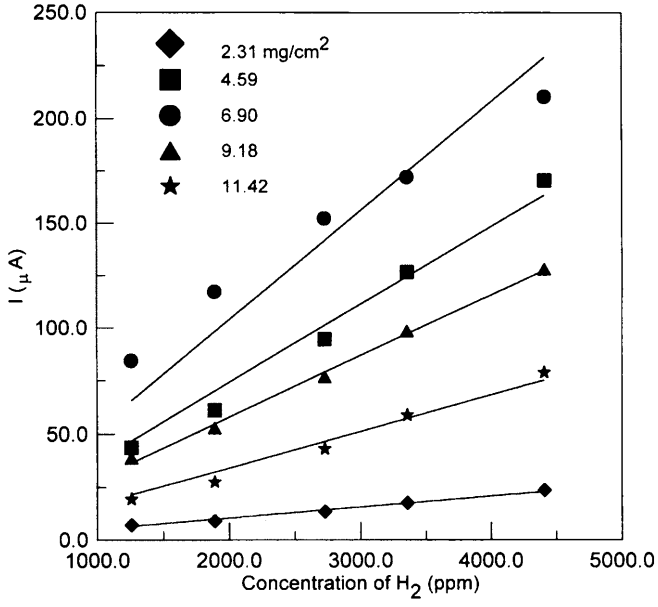

Fig. 7 Detected steady current of a Pd/Nafion electrode as a function of the hydrogen concentration

sistent with the investigation by the SEM of the active surface area. It also supports that the deposited Pd becomes a more compact layer when the Pd loading exceeds the optimum, which results in a lower active surface area.

Response and recovery times

Actually, the response and recovery times in gas sensing with a fixed hydrogen concentration are determined by two factors: the pore volume (V) of the electrodes and the active surface area (A) of the deposited Pd. A smaller pore volume means less hydrogen retained. Therefore, shorter response and recovery times for hydrogen oxidation will be obtained. Meanwhile, a larger active surface area undoubtedly contributes to a fast response, and a shorter recovery time is expected owing to a lesser quantity of hydrogen remaining. Thus, both the response and the recovery times are directly proportional to the term V/A.

Figure 9 shows the effect of H_2 concentration on the response and recovery times at 0.06 M $NaBH_4$, which corresponds to the shortest response and recovery times. These can be explained by the SEM and the XRD observations and the results of the active surface area, as discussed previously. Increasing the $NaBH_4$ concentration results in a smaller deposited Pd size and forms a more compact layer on the Nafion film. Therefore, an optimum active surface area is obtained at 0.06 M $NaBH_4$. However, the effects of the particle size and the compactness of the deposited Pd on Nafion at a fixed Pd loading on the pore volume are ambiguous. Consequently, the fastest response and recovery times occur at an optimum of 0.06 M $NaBH_4$, which corresponds to a maximum active surface area. Generally, the H_2 concentration has no influence on the response and recovery times on a modified Nafion electrode with uniform Pd coverage. However, the response time decreases with an increase of the hydrogen concentration, but the recovery time increases with an increase of the hydrogen concentration, as shown in Fig. 9. It is likely that the higher H_2 concentration implies that more hydrogen molecules can exist deeper in the Nafion film. This results in increasing the average active surface area available. Thus, the higher H_2 concentration is responsible for a faster

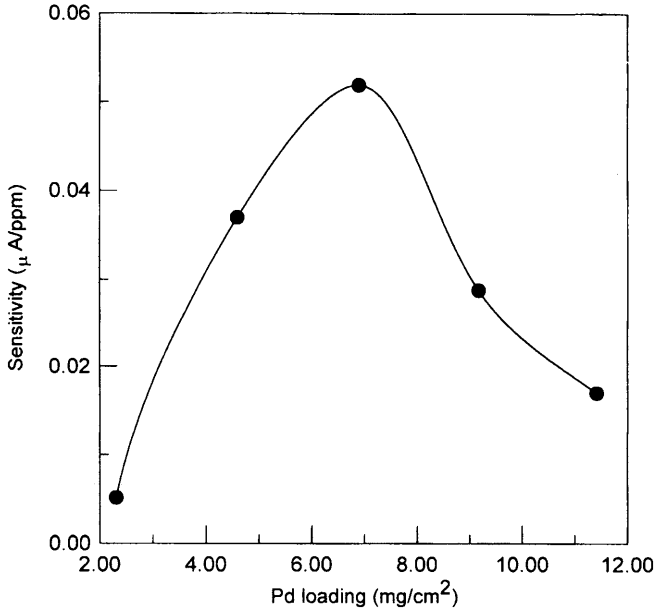

Fig. 8 Detected steady current of Pd/Nafion electrode prepared at 0.06 M $NaBH_4$ as a function of the quantity of Pd loading in 2730 ppm H_2

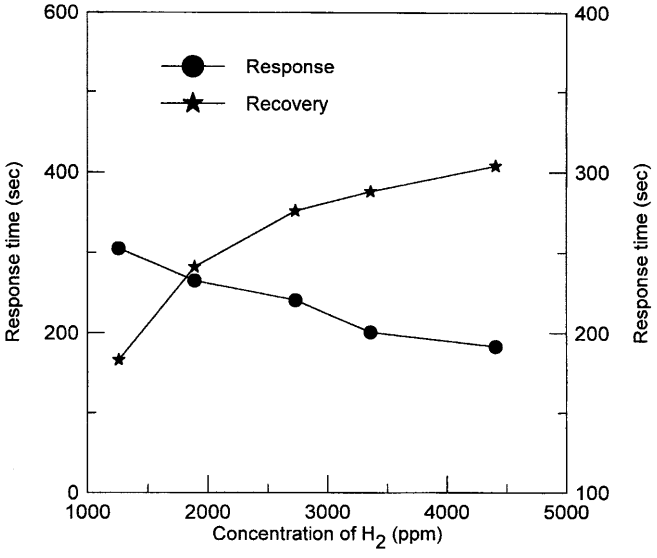

Fig. 9 Response and recovery time for various concentrations of H_2 on a Pd/Nafion electrode prepared at 0.006 M $Pd(NH_3)_4Cl_2$ and 0.06 M $NaBH_4$

Table 1 Response and recovery time for various concentrations of H_2 on a Pd/Nafion electrode prepared at 0.06 M $NaBH_4$ and different Pd loadings

H_2 concentration (ppm)	Response time (s)/recovery time (s)				
	Pd loading (mg/cm^2)				
	2.31	4.59	6.90	9.18	11.42
1260	398/215	395/214	305/183	260/153	240/92
1890	382/262	350/254	265/241	190/195	180/156
2730	371/378	330/288	241/276	159/204	156/158
3360	364/471	270/301	201/288	149/225	140/160
4410	350/581	250/328	183/304	138/270	123/206

response time. On the other hand, there remains a relatively high quantity of unreacted hydrogen in the deeper layer in a higher H_2 concentration experiment after the sensed gas is turned off. Therefore, it is difficult for the remaining hydrogen to diffuse out from the deeper layer of the Nafion film. Thus, a longer recovery time is expected to a steady state in a higher H_2 concentration experiment.

Table 1 demonstrates the effects of Pd loading on the response and recovery times at various H_2 concentrations. The H_2 concentration exhibits the similar influence on the response and recovery times as observed in Fig. 9. Clearly, increasing the Pd loading would decrease the pore volume of the Nafion film. This results in shortening the response and recovery times. Meanwhile, the effect of the quantity of Pd loading on the active surface area exhibits an optimum condition at a Pd loading of 6.90 mg/cm^2 as mentioned before. Otherwise, the active surface area decreases when the Pd loading exceeds the optimum. However, the response and recovery times are directly proportional to the term V/A. The influence of the pore volume is more significant than that of the active surface area at the Pd loading exceeding the optimum. Thus, the response and recovery times decrease with an increase of the Pd loading, as shown in Table 1.

Conclusion

The Pd/Nafion electrodes prepared by an impregnation-reduction method were employed for sensing hydrogen. There exists an optimum condition for both the reductant concentration of $NaBH_4$ and the quantity of Pd loading to obtain the maximum active surface area and sensitivity for sensing hydrogen. The maximum sensitivities on the Pd/Nafion electrode with a Pd loading of 6.90 mg/cm^2 prepared at 0.006 M $Pd(NH_3)_4Cl_2$ and 0.06 M $NaBH_4$ are 0.0519 μA/ppm, obtained in H_2 concentrations of 0–4410 ppm. Pd/Nafion electrodes with a Pd loading of 11.42 mg/cm^2, obtained with 0.01 M $Pd(NH_3)_4Cl_2$ and 0.06 M $NaBH_4$, show the fastest response and recovery times in sensing hydrogen. Generally, the response time decreases with an increase of the hydrogen concentration, but the recovery time increases with an increase of the hydrogen concentration. A sensing model was proposed to illustrate the relationship between the characteristics of the electrodes and their sensing performances.

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