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Nafion-based solid-state gas sensors: Pt/Nafion electrodes prepared by an impregnation-reduction method in sensing oxygen

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Abstract The influences of the reductant concentration of NaBH_4 and the quantity of Pt loading on the active surface area and the sensitivity of the Pt/Nafion electrodes prepared by an impregnation-reduction method in detecting oxygen were investigated in this study. The Pt/Nafion electrodes with a Pt loading of 4.99 mg/cm^2 , obtained at $0.0107 \text{ M Pt}(\text{NH}_3)_4\text{Cl}_2$ and 0.06 M NaBH_4 , show maximum sensitivities of $0.0528 \text{ } \mu\text{A/ppm}$ and $0.0538 \text{ } \mu\text{A/ppm}$ obtained in O_2 concentration regions of $0\text{--}5000$ and $5000\text{--}50\,000$ ppm, respectively. A sensing model was also proposed to illustrate the sensing phenomenon.

Key words Impregnation-reduction method
Pt/Nafion · Sensitivity

Introduction

Recently, many researchers have attempted to develop solid-state gas sensors which can be operated at room temperature [1–4]. The advantage of a solid polymer electrolyte (SPE) is that no liquid electrolyte is required in sensing gas. This can simplify product separation and purification, diminish side reactions, permit the construction of miniature detectors and avoid detectors being damaged by the leaking of liquid electrolytes and corrosion [5]. Nafion, a copolymer of tetrafluoroethylene and sulfonyl fluoride vinyl ether cation exchange membrane, is one of the famous SPEs widely used in the development of sensors. It has excellent ionic conductivity, good permselectivity, outstanding chemical and thermal stability, and good mechanical strength [6, 7]. Moreover, Nafion modified by means of metalization,

especially with noble metals, can form composite materials with ionic and electronic conductivity characteristics, which are very important in gas sensing. The metalized Nafion is of particular interest for such a goal. The metalization methods reported previously in the literature can be classified as (1) mechanical processes [8, 9], (2) electrochemical processes [10, 11], (3) vacuum sputtering processes [12, 13], and (4) chemical reduction processes [14, 15]. The chemical reduction methods mentioned above could be 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], this has aroused great interest recently.

This paper presents an amperometric detector for sensing oxygen on a Pt-modified Nafion prepared by an I-R method. The influences of the reductant concentration of NaBH_4 and the quantity of the Pt loading on the active surface area and the sensitivity of the electrodes for detecting oxygen were examined. The relationship between the characteristics of the Pt/Nafion electrodes and their sensing performance was also investigated.

Experimental design

Pt deposition onto Nafion by an I-R method

A piece of $25 \times 25 \text{ mm}$ and 0.0432-mm -thick Nafion 117 (Du Pont, cation exchange type) was boiled in $3\% \text{ H}_2\text{O}_2$ for 40 min and then rinsed with distilled water. The Nafion film was dipped in 9 M HCl at $80 \text{ }^\circ\text{C}$ for 50 min to exchange it for 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 Pt layer was obtained by exposing only one side of the membrane to a $0.0107 \text{ M Pt}(\text{NH}_3)_4\text{Cl}_2$ solution fixed at pH 11.5 for 3h, followed by washing the impregnated membrane with distilled water and then exposing it again for another 2h to an alkaline solution with NaBH_4 as the reductant. The experimental temperature was maintained at $35 \text{ }^\circ\text{C}$

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with a water bath. The Pt loading was determined from the difference of the concentrations of $\text{Pt}(\text{NH}_3)_4^{2+}$ before and after depositing Pt onto the Nafion film, via the atomic adsorption spectrophotometer. Thus, the various $\text{Pt}(\text{NH}_3)_4^{2+}$ concentrations of 0.0054, 0.0075, 0.0107, 0.0129, and 0.015 M corresponding to Pt loadings of 2.48, 3.66, 4.99, 5.82, and 7.41 mg/cm^2 , respectively, were obtained from 0.06 M NaBH_4 . Scanning electron microscopy (SEM) and X-ray diffraction (XRD) were used to examine the morphology and crystal size of the deposited Pt, and the depth profiles of Pt deposited onto the film were analysed by performing secondary ion mass spectrometry (SIMS) experiments.

Electrochemical characteristics

All electrochemical experiments were performed via a potentiostat (Model 273A, EG&G) with a sensor geometric surface of 0.238 cm^2 at ambient temperature. The active surface area of Pt deposited onto Nafion electrodes was determined from the hydrogen desorption region during cyclic voltammetry experiments in 1M H_2SO_4 at a sweep rate of 100 mV/s [21, 22]. The electrochemical cell comprised two compartments. The Pt/Nafion composite behaved as a separator dividing the anode and cathode compartments. The cathodic reduction of oxygen was carried out in the divided cells with Pt/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 1 M H_2SO_4 and test gases, respectively. The various concentrations of oxygen in the O_2 - N_2 mixtures were prepared using a mass-flow-rate controller (Model 840 Mass Meter) and were expressed in ppm (v/v) O_2 . Polarization curves were obtained using a potentiostat, as mentioned above.

Results and discussion

Characteristics of the Pt/Nafion electrodes

Figure 1 shows the SEM photographs of a Nafion film and Pt/Nafion electrodes prepared by the I-R method with various reductant concentrations of NaBH_4 . The results indicate that columnar-shaped and granular-shaped particles were formed at lower and higher concentrations of the reductant, respectively. The particle size decreases with increasing reductant concentration, at both lower and higher concentrations. It implies that the nucleation rate of Pt formation increases with reductant concentration. The Pt/Nafion electrodes become more compact with increase in reductant concentration.

The depth profile of the Pt/Nafion electrode indicated in Fig. 2 reveals that the thickness of film is about 0.8 μm in depth. Figure 3 shows the X-ray diffraction patterns of the Pt/Nafion electrodes. Their crystalline (111) orientation is found to be dominant and independent of the reductant concentration. The crystalline diameter (d) can be estimated from the following equation [21]:

$$d = \frac{0.9 \lambda}{B \cos \theta_B} \quad (1)$$

where λ , B , and θ_B are the wavelength of the weighted average K_α value of the Cu target, the angular width of half-maximum line breadth, and the half-degree of the peak, respectively. The results are obviously correlated

with the degree of the reductant concentration, as shown in Table 1. This indicates that the average crystalline diameter decreases with an increase in the reductant concentration. Figure 4 demonstrates the cyclic voltammogram of the Pt/Nafion electrode at a scan rate of 100 mV/s with the anode and cathode compartments filled with nitrogen and 1 M H_2SO_4 , respectively. The actual active surface area of the deposited Pt could be estimated from the charge of the peak area of hydrogen desorption divided by the factor of 210 $\mu\text{C}/\text{cm}^2$ [22, 23]. The data reveal that the Pt/Nafion electrode prepared with 0.06 M reductant has the maximum active surface area. Inspection of Figs. 5 and 6 allows us to evaluate the effects of the Pt loading and reductant concentrations of NaBH_4 on the active area and roughness factor. As shown in Fig. 5, the maxima of the active area and roughness factor were obtained at a Pt loading of 4.99 mg/cm^2 , corresponding to an optimum condition for sensing gas. Similar phenomena have been observed in the study of Fedkim and Her in sensing hydrogen [24]. The results in Fig. 6 show the maxima of the active area and roughness factor at 0.06 M NaBH_4 , which is an optimum reductant concentration for preparing Pt/Nafion electrodes. This indicates that the electrode will become too compact when the quantity of Pt loading or the NaBH_4 concentration exceeds the optimum. These are consistent with the observations in the SEM pictures (Fig. 1). Meanwhile, these results are also consistent with the observation of the sensor's performance, which will be discussed later.

Current-potential relation

Figure 7 shows the current-potential relationship of the Pt/Nafion electrode in the presence and absence of oxygen. It indicates that the oxygen reduction reaction occurs at a potential of 0.2 V vs Ag/AgCl. At a more negative cathodic potential, the reduction current increases sharply. It results from the hydrogen evolution reaction in an aqueous solution whose interference renders the ambiguous potential region with a limiting current of oxygen reduction. To extract the sensing current of oxygen from the total current involving hydrogen evolution and oxygen reduction reactions, the current difference in the presence and absence of oxygen was plotted against the potential, as shown in Fig 8. As can be seen in this figure, there is a maximum at a potential of -0.15 V vs Ag/AgCl. This implies that the interference from hydrogen evolution is a minimum at this potential. Consequently, this polarization potential was chosen to protect the sensing current from the interference of hydrogen evolution in this work.

Linearity and sensitivity

The response current of the sensors can be controlled by the diffusion rate of bulk oxygen in the gas boundary

Fig. 1a–e SEM images of Pt/Nafion electrodes prepared by the impregnation-reduction (I-R) method with various reductant concentrations of NaBH_4 : **a** 0.02 M, **b** 0.04 M, **c** 0.06 M, **d** 0.08 M, **e** 0.1 M

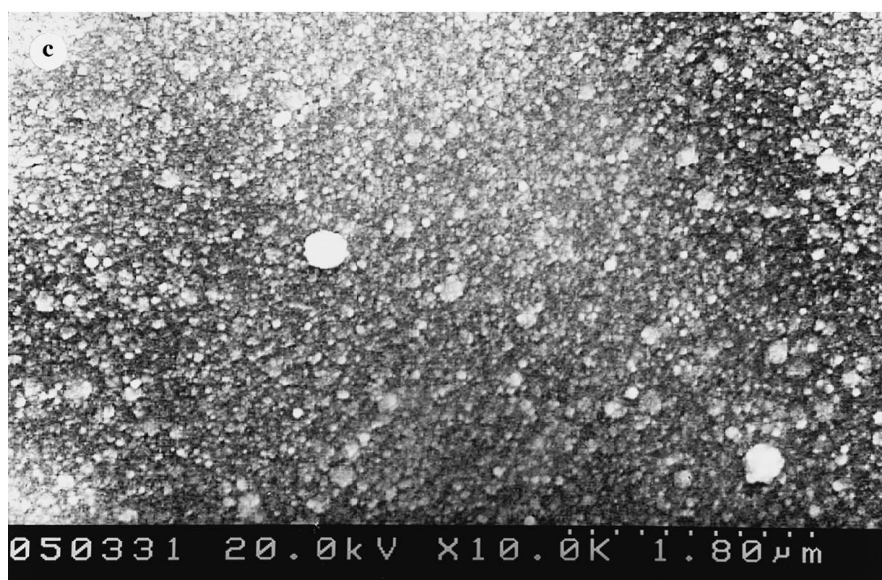
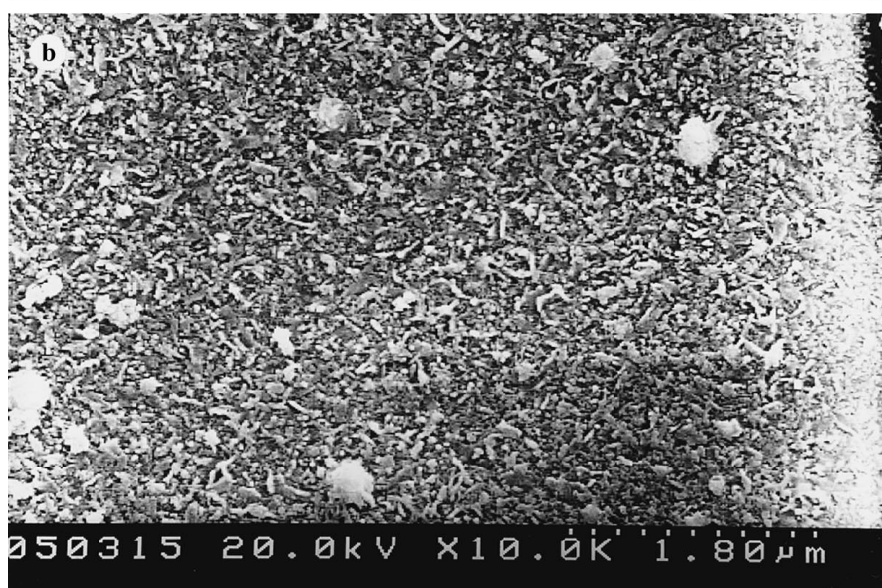
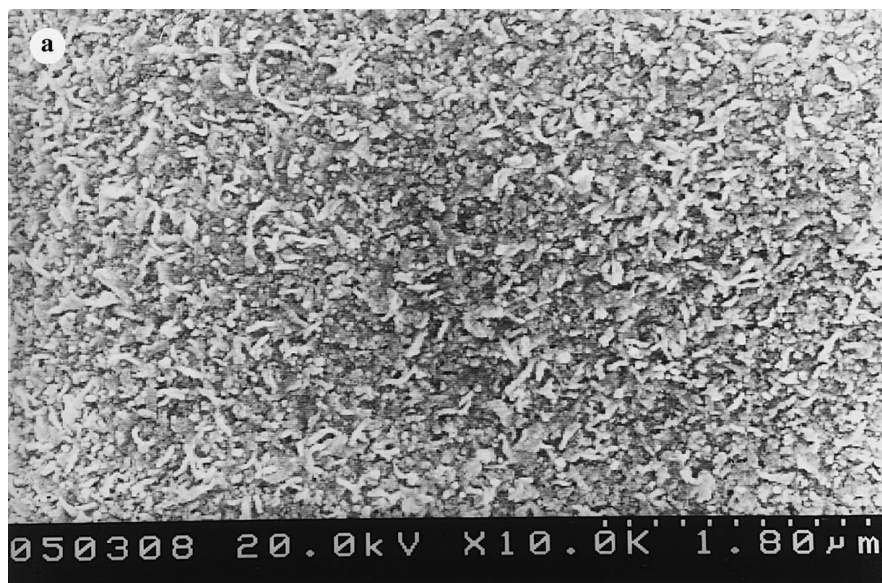
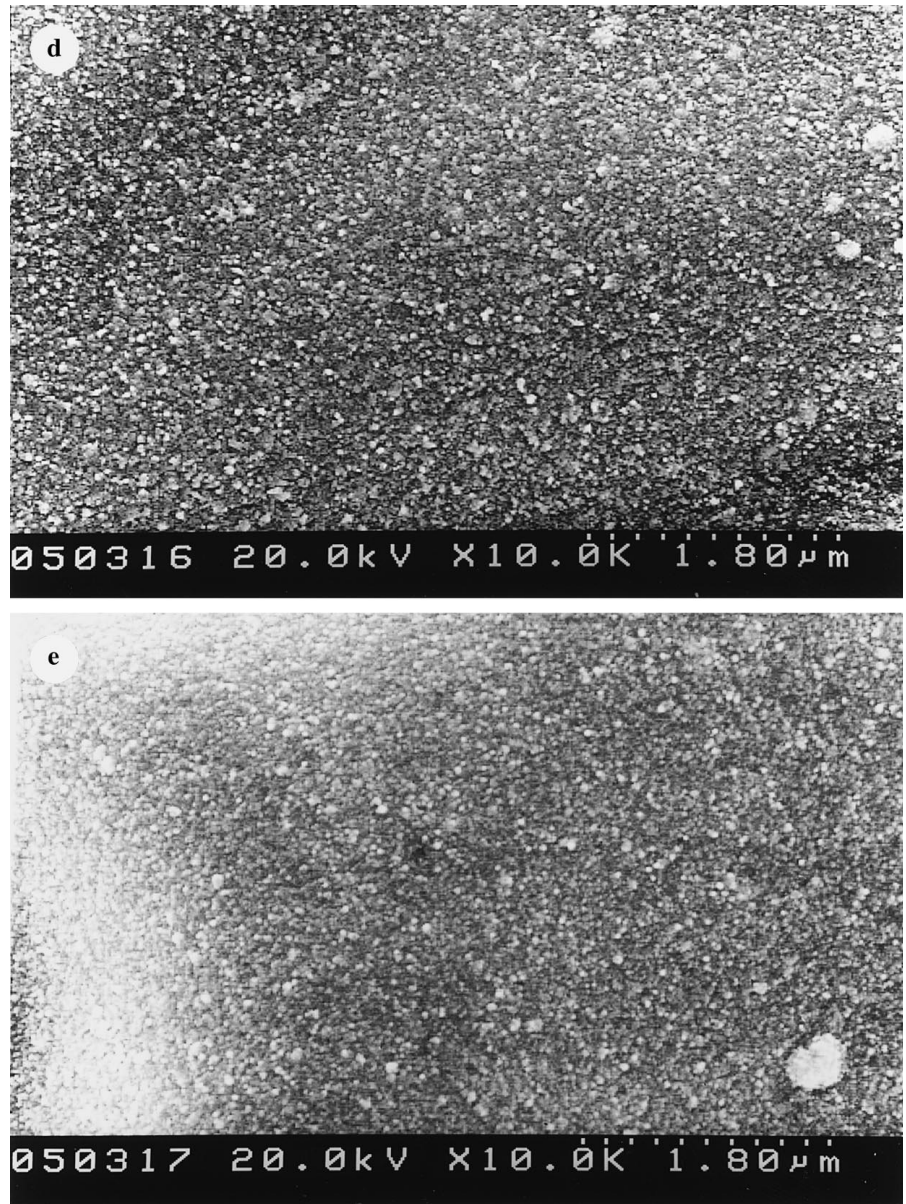


Fig. 1d, e



layer (r_1) and by the reduction rate of oxygen (r_2) at active sites within the Pt/Nafion layer, as indicated in Fig. 9. The reaction kinetics can be expressed by:

$$r_1 = k_m (C_b - C_s) \quad (2)$$

$$r_2 = k_s \eta C_s \quad (3)$$

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 O_2 concentration and the interfacial O_2 concentration between the gas and the Pt/Nafion layer, respectively. The catalytic effectiveness factor [25] can be expressed as

$$\eta = (3/\Phi^2)(\Phi \coth \Phi - 1) \quad (4)$$

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

$$\Phi = L(k_s S_a \rho_p / D_e)^{1/2} \quad (5)$$

where L , S_a , ρ_p , k_s , and D_e are the thickness of the Pt 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 can lead to an increase in this term. However, the effective diffusivity decreases when the electrode becomes more compact.

At steady state, the response current of the sensor system can be derived from Eqs. 2 and 4 and be given as

$$i = nFA \frac{1}{\frac{1}{k_m} + \frac{1}{k_s \eta}} C_b \quad (6)$$

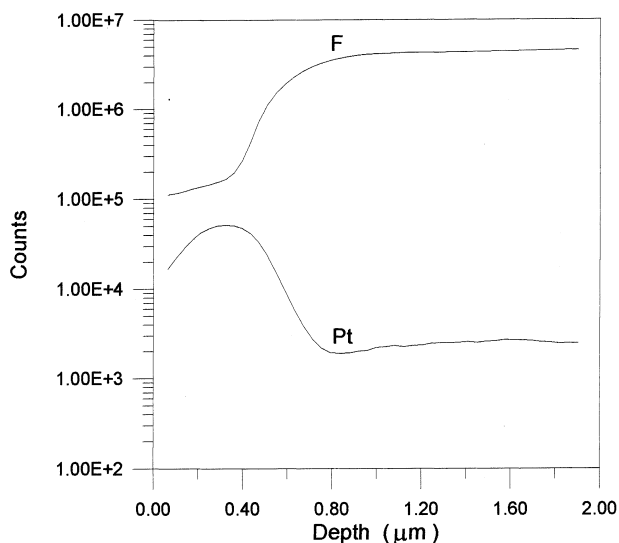


Fig. 2 Depth profile of the Pt/Nafion electrode prepared by the I-R method using 0.0107 M $\text{Pt}(\text{NH}_3)_4\text{Cl}_2$ and 0.06 M NaBH_4

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

$$S = \frac{nFA}{\frac{1}{k_m} + \frac{1}{k_s\eta}} \quad (7)$$

Since the sensing current is independent of the gas flow rate at an oxygen concentration of 25 750 ppm (data not shown here), it implies that the external diffusion resistance ($1/k_m$) can be neglected in this case and therefore Eq. 7 can be simplified as

$$S = nFAk_s\eta \quad (8)$$

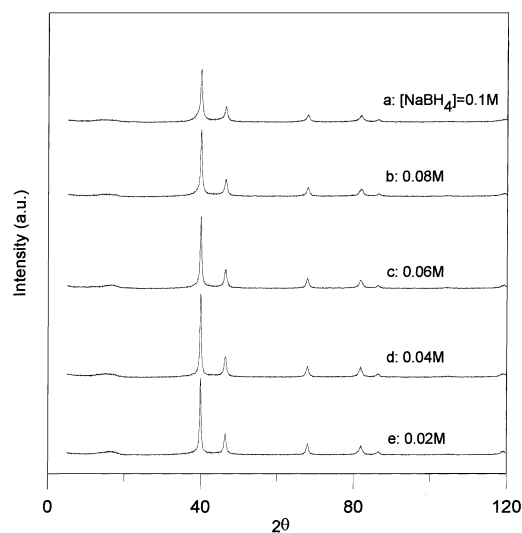


Fig. 3 XRD patterns of Pt/Nafion electrodes prepared with 0.0107 M $\text{Pt}(\text{NH}_3)_4\text{Cl}_2$ and various reductant concentrations of NaBH_4 : a 0.02 M, b 0.04 M, c 0.06 M, d 0.08 M, e 0.1 M

Table 1 Average crystalline diameter of the Pt/Nafion electrodes prepared at 0.0107 M $\text{Pt}(\text{NH}_3)_4\text{Cl}_2$ and various reductant concentrations

Conc. of NaBH_4 (M)	40° (111) d (Å)	46° (200) d (Å)	68° (220) d (Å)	82° (311) d (Å)
0.02	103.58	89.36	82.52	82.91
0.04	92.01	78.14	86.40	81.45
0.06	88.23	83.60	110.95	111.12
0.08	81.02	67.96	84.70	83.88
0.10	74.91	77.26	90.74	86.27

Figure 10 shows the response curves at various concentrations of oxygen on Pt/Nafion electrodes with different Pt loadings. As shown in the response curves, increasing the concentration of oxygen leads to an increase in the sensing current. However, the sensing current increases and then decreases with increasing Pt loading. Figure 11 exhibits the detected steady currents of Pt/Nafion electrodes with different Pt loadings at various O_2 concentrations. The slope of the straight line represents the sensitivity of the oxygen sensor on Pt/Nafion electrodes. Two linear relationships between the sensing current and oxygen concentration can be observed at the regions of low and high oxygen concentrations, respectively. This suggests that the external diffusion resistance cannot be completely neglected at low concentrations of oxygen. Consequently, the sensitivity at low concentrations of oxygen is slightly lower than that at high concentrations of oxygen.

The sensitivities increase with an increasing quantity of Pt loading up to a maximum value and then decrease when the Pt loading is over the optimum value, as shown in Fig. 12. The reason for this can be explained from the inspection of Eq. 7. The surface area of the Pt/Nafion electrodes (A) increases with an increase in Pt loading.

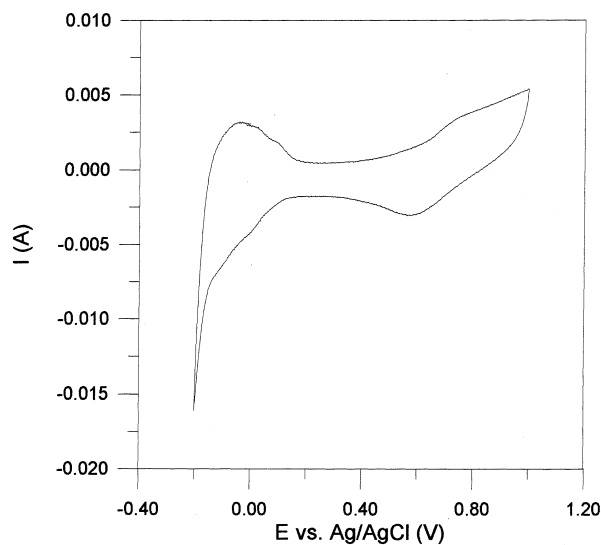


Fig. 4 A typical cyclic voltammogram of the Pt/Nafion electrode prepared by the I-R method using 0.0107 M $\text{Pt}(\text{NH}_3)_4\text{Cl}_2$ and 0.06 M NaBH_4

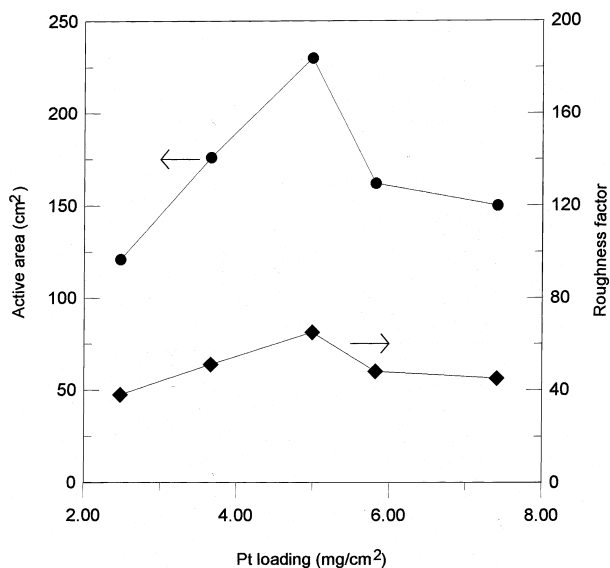


Fig. 5 Active surface area and roughness factor of the Pt/Nafion electrodes prepared with 0.06 M NaBH₄ and various Pt loadings

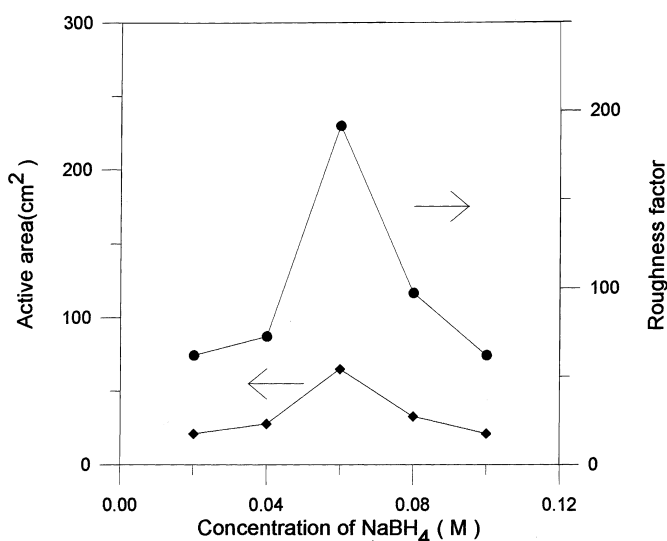


Fig. 6 Active surface area and roughness factor of the Pt/Nafion electrodes prepared with various reductant concentrations of NaBH₄ and 0.0107 M Pt(NH₃)₄Cl₂

The electrodes become more compact; therefore the effective diffusivity decreases when the Pt loading increases. From Eq. 5, increasing A ($S_a \rho_p$) and decreasing D_e with an increase in Pt loading leads 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 Pt loading. Since the mass transfer coefficient k_m is negligible, the overall reaction is dominated by the internal diffusion resistance within the Pt/Nafion electrode. Therefore, the sensitivity is directly proportional to the value of $nFAk_s\eta$, as expected. As shown in Fig. 12, the sensitivities increase significantly from 0.0215 to a maximum of 0.0528 $\mu\text{A}/$

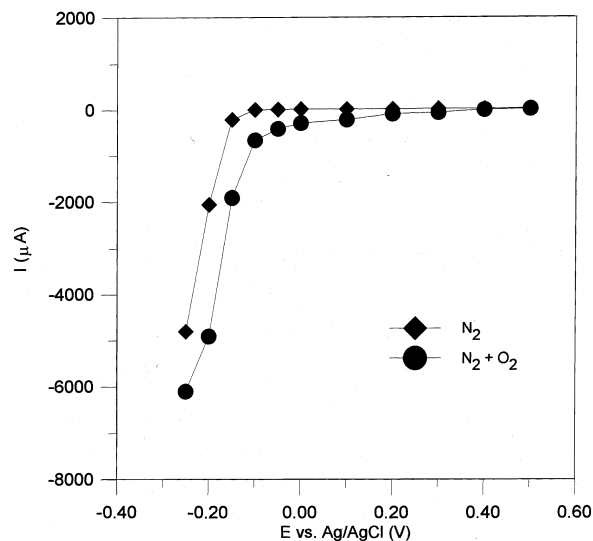


Fig. 7 Polarization curves for a Pt/Nafion electrode in the presence of 41 200 ppm O₂ and in the absence of O₂

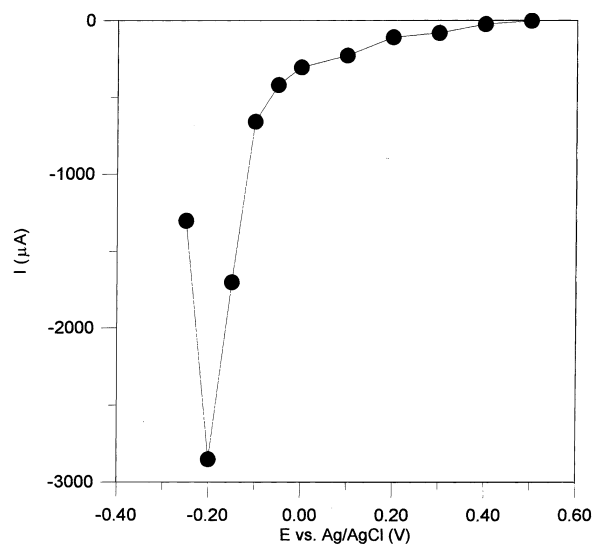


Fig. 8 Current difference in the presence and absence of O₂

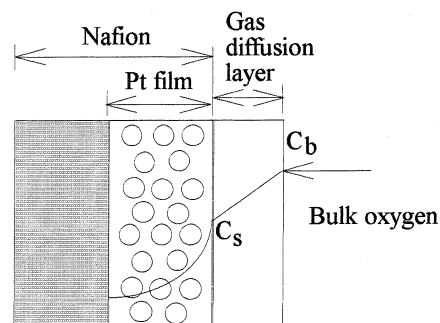


Fig. 9 The concentration profiles of O₂ in the sensing system of a Pt/Nafion electrode

ppm with an increase in Pt loading from 2.48 to 4.99 mg/cm², but decrease suddenly with a further increase in Pt loading in O₂ concentrations of 0–5000 ppm.

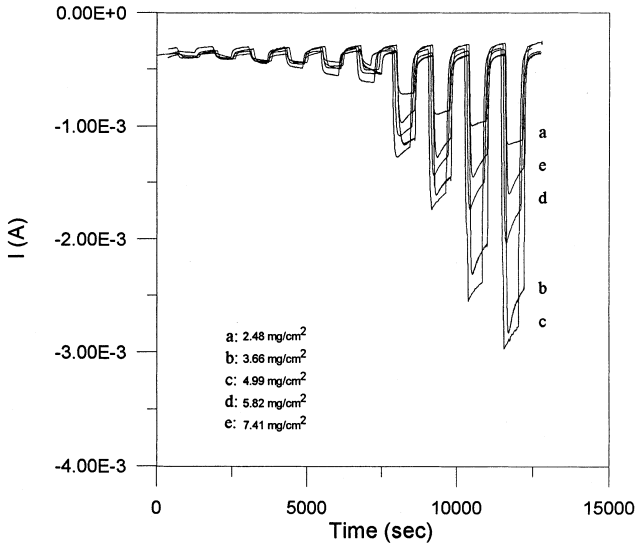
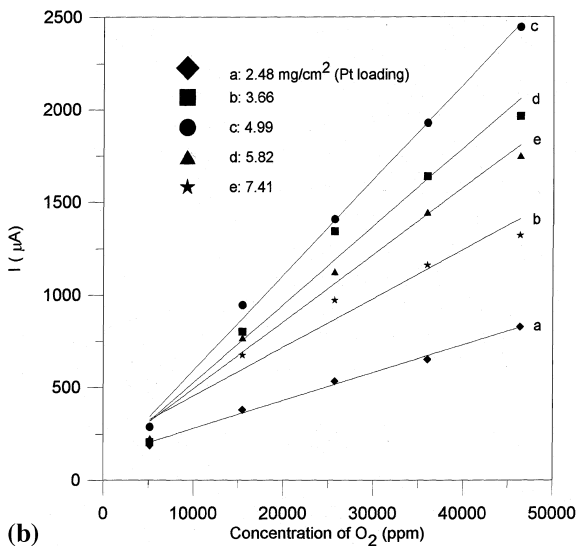
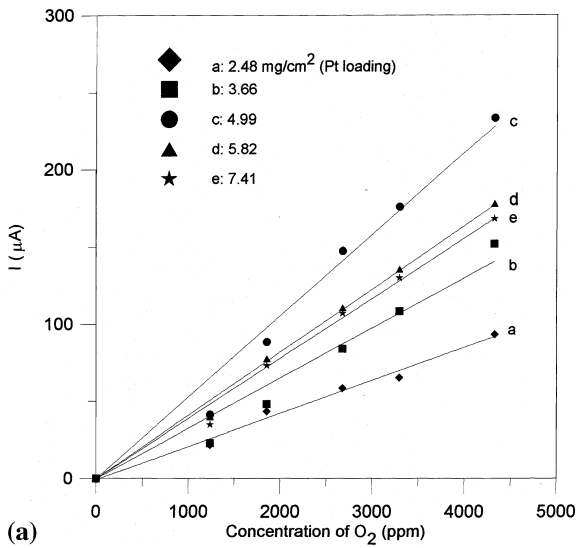


Fig. 10 Response curves for various concentrations of O₂ on a Pt/Nafion electrode with different Pt loadings



In O₂ concentrations of 5000–50 000 ppm, the same phenomenon is observed with a maximum sensitivity of 0.0538 µA/ppm at a Pt loading of 4.99 mg/cm². The results are consistent with the investigation of the SEM and active surface area. It supports the view that the deposited Pt becomes a more compact layer when the Pt loading exceeds the optimum, which results in a lower active surface area.

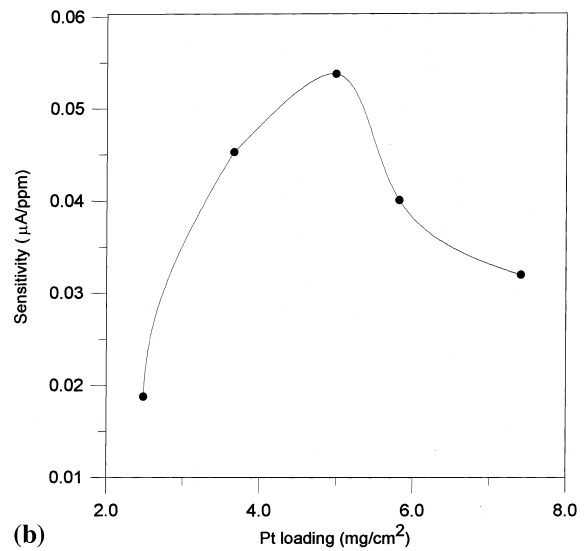
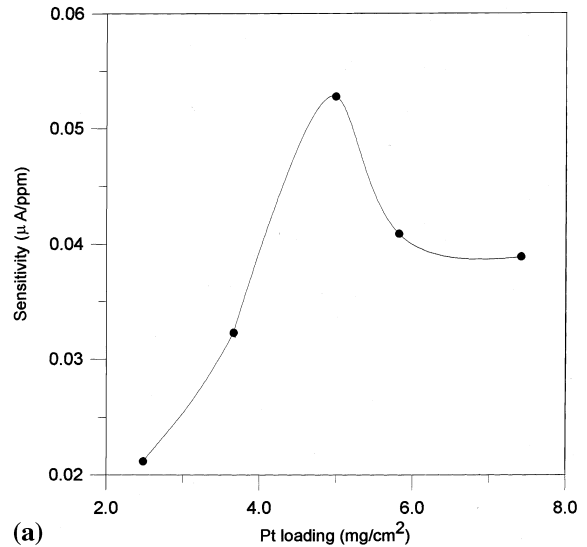


Fig. 12a, b Detected steady current of a Pt/Nafion electrode as a function of the quantity of Pt loading: a 0–5000 ppm O₂; b 5000–50 000 ppm O₂

Fig. 11a, b Detected steady current of a Pt/Nafion electrode as a function of O₂ concentration: a 0–5000 ppm; b 5000–50 000 ppm

Conclusion

The Pt/Nafion electrodes prepared by an impregnation-reduction method were employed for sensing oxygen. There exists an optimum condition for both the reductant concentration of NaBH₄ and the quantity of Pt loading to obtain the maximum active surface area and sensitivity for sensing oxygen. The maximum sensitivities on the Pt/Nafion electrode with a Pt loading of 4.99 mg/cm² prepared at 0.0107 M Pt(NH₃)₄Cl₂ and 0.06 M NaBH₄ are 0.0528 μA/ppm and 0.0538 μA/ppm obtained in O₂ concentration regions of 0–5000 and 5000–50 000 ppm, respectively. A sensing model was proposed to illustrate the relationship between the characteristics of the electrodes and their sensing performances.

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