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Characteristics of Pd/Nafion oxygen sensor modified with polypyrrole by chemical vapor deposition

Abstract In this study, Pd/Nafion electrodes were prepared by impregnation-reduction methods in sensing oxygen. To prolong the electrode's life in practical use, a polypyrrole (PPy) film was chemically deposited onto the Pd/Nafion electrode. The sensitivities of PPy-modified Pd/Nafion electrodes are 0.00671 and 0.0117 µA/ppm obtained in O_2 concentration regions of 0–5000 and 5000–50,000 ppm, respectively. Generally, the response time and the recovery time decreases and increases significantly with increasing O_2 concentrations. After continuous aging tests for 48 h, the sensitivities of the Pd/Nafion and the PPy-modified Pd/Nafion electrodes decrease by 97% and 53%, respectively.

Keywords PPy-modified Pd/Nafion electrode · Chemical vapor deposition · Aging · Oxygen

Introduction

Recently, the development of solid-state gases sensors, which can be operated at ambient temperature, has received considerable attention [1, 2, 3, 4]. The solid polymer electrolyte (SPE) owns the advantage of no liquid electrolyte being required in sensing gas. This can simplify product separation and purification, diminish side reactions, permit the construction of miniature, and avoid detectors being damaged by leaking of liquid electrolytes and corrosion [5]. Nafion (Du Pont de Nemours and company), a perfluorated cation-exchange membrane, is one of the best known SPE materials widely used in the development of sensors. It has an excellent ionic conductivity, a good permselectivity, an outstanding chemical and thermal stability, and a good mechanical strength [6, 7]. Moreover, Nafion modified by means of metalization, especially with noble metals, can become composite materials with ionic and electronic conductivity characteristics, which are very important in sensing gas. The metalized Nafion is of particular interest for such a goal. The metalization methods reported in previous literature include mechanical [8, 9], electrochemical [10, 11], vacuum sputtering [12, 13], and chemical reduction [14, 15] processes. The chemical reduction methods mentioned above could be divided into two different kinds: the Takenata-Torikai method (T-T method) [6, 16] and the impregnation-reduction method (I-R method) [17, 18]. Since a mechanically stable electrode with a high surface area can be easily obtained from a chemical reduction process [19], this has aroused great interest recently.

Recently, we have published some papers concerning the characteristics of Nafion electrodes metalized via T-T and I-R methods in sensing oxygen [20, 21, 22]. However, how to overcome the aging problem of detectors in sensing gases is also interesting, especially in practical use. This work presents a new amperometric oxygen sensor using Pd/Nafion electrodes coated with polypyrrole (PPy) films by a chemical vapor deposition (CVD) method. The characteristics and the anti-aging ability of the PPy-modified Pd/Nafion electrodes were investigated. Also, a sensing model was proposed to illustrate the sensing phenomenon.

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Experimental

Preparation of PPy-modified Pd/Nafion

The pretreatment of Nafion membrane and the preparation procedure of Pd -metalized Nafion (called Pd/Nafion) by an I-R method were shown in the previous study [20]. The Pd loading on

Nafion was fixed at 6.9 mg/cm^2. Then the Pd/Nafion was spin-coated with 0.05 mol/l FeCl$_3$ oxidant, followed by CVD PPy from an acetonitrile solution containing 1.3 mol/l pyrrole for 5 min (called PPy-modified Pd/Nafion).

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. Oxygen reduction was carried out with PPy-modified or pure Pd/Nafion as the working electrode, a Pt/Ti gauze as the counter electrode, and a saturated Ag/AgCl electrode as the reference. The cathode and anode chambers were filled with oxygen and 1 mol/l H$_2$SO$_4$, respectively. The various concentrations of oxygen in the O$_2$-N$_2$ mixture was determined using a mass-flow-rate controller (Model 840 Mass Meter) and were expressed in ppm (v/v) O$_2$.

Results and discussion

Current-potential relation

Figure 1 shows the current-potential relationship of the PPy-modified Pd/Nafion electrode in the presence and absence of oxygen. It indicates that oxygen reduction reaction occurs with the potential toward the cathodic one. 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 potential region with limiting current of oxygen reduction ambiguous. 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
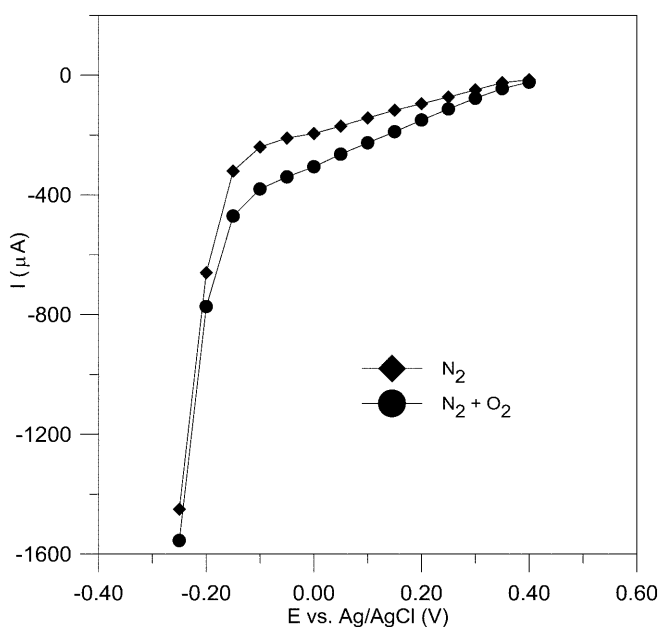
shown in Fig. 2. As can be seen in this figure, there is a maximum at the potential of –0.15 V vs Ag/AgCl. It implies that the interference of hydrogen evolution is minimum at this potential. Consequently, this polarization potential was chosen to protect the sensing current from the interference of hydrogen evolution in this work.

Linearity and sensitivity

The response current of the sensors is controlled by the diffusion rate of bulk oxygen in the gas boundary layer (r$_1$) and by the reduction rate of oxygen (r$_2$) at active sites within the Pd/Nafion layer, as indicated in Fig. 3. The reaction kinetics can be expressed by

$$r_1 = k_m(C_b - C_s) \tag{1}$$
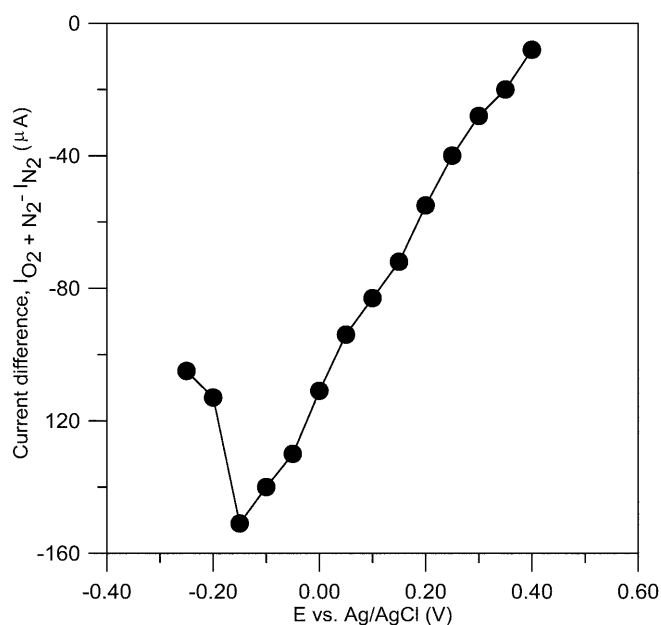
$$r_2 = k_s \eta C_s \tag{2}$$

Fig. 2 Current difference in the presence and absence of oxygen
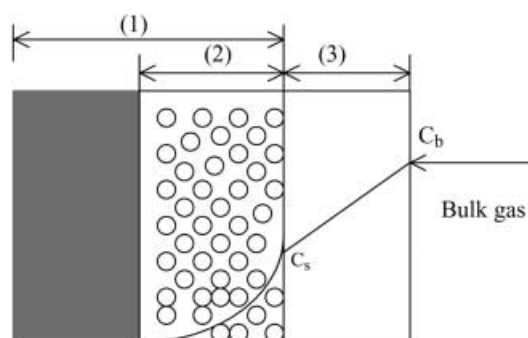

Fig. 3 The concentration profiles of oxygen in the sensing system of a PPy-modified Pd/Nafion electrode: (1) Nafion electrode; (2) Pd film; (3) gas diffusion layer in PPy film

Fig. 1 Polarization curves for a PPy-modified Pd/Nafion electrode in the presence of 25750 ppm O$_2$ and absence of O$_2$

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 O_2 concentration and the interfacial O_2 concentration between the gas and the Pd/Nafion layer, respectively. The catalytic effectiveness factor [23] can be expressed as

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

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

$$\Phi = L(k_s S_a \rho_p / D_e)^{1/2} \qquad (4)$$

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

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

$$i = nFA \frac{1}{\frac{1}{k_m} + \frac{1}{k_s\eta}} C_b \qquad (5)$$

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

$$S \frac{nFA}{\frac{1}{k_m} + \frac{1}{k_s\eta}} \qquad (6)$$

Since the sensing current is independent of the gas flow rate at oxygen concentration of 25750 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

$$S = nFAk_s\eta \qquad (7)$$

Figure 4 demonstrates a continuous responses curve on the PPy-modified Pd/Nafion electrode at oxygen concentration of 25,750 ppm. As shown in this response curve, the sensing current rises reproducibly in the presence of the test gas and the background current recovers well in the absence of the test gas. This indicates that the PPy-modified Pd/Nafion electrode senses stably. Figure 5 shows the detected steady currents on the PPy-modified Pd/Nafion electrode at various oxygen concentrations. The slope of the straight line represents the sensitivity of electrodes for oxygen sensing. Two linear relationships between the sensing current and oxygen concentration with sensitivities of 0.00671 and 0.0117 µA/ppm can be observed at the regions of low and high oxygen concentrations, respectively. This sug-
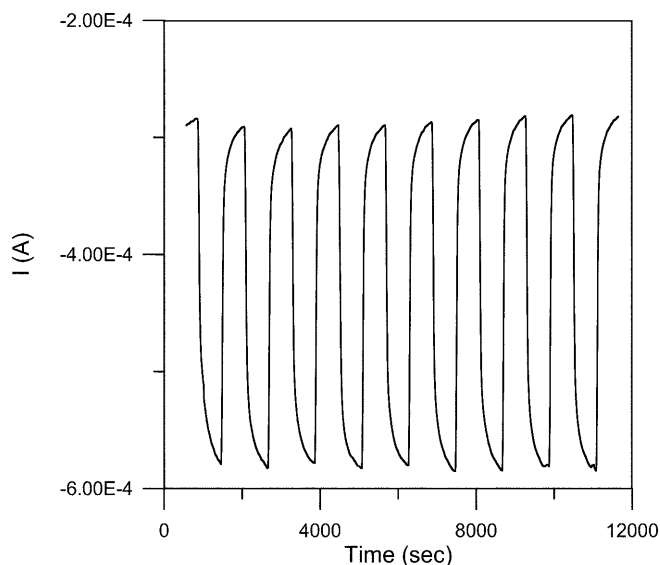

Fig. 4 Continuous responses curve on the PPy-modified Pd/Nafion electrode at oxygen concentration of 25,750 ppm

gests that the external diffusion resistance cannot be completely neglected at low concentration of oxygen. Consequently, the sensitivity at low concentration of oxygen is slightly lower than that at high concentration of oxygen.

Response and recovery time

The response and the recovery times in sensing at a fixed oxygen 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 oxygen remains in the sensor; therefore a shorter response and recovery time will be obtained. A large active surface area undoubtedly contributes to a fast response, and a shorter recovery time, for the same reason. Thus, both the response and the recovery times are directly proportional to V/A.

Figures 6 and 7 show the effects of oxygen concentration on the response and recovery times, respectively, on the PPy-modified Pd/Nafion electrodes. Generally, oxygen concentration has no influence on the response and recovery times of a uniform electrode. However, the results indicate that the response time decreases with an increase of O_2 concentration, as shown in Fig. 6, but the recovery time increases with an increase of O_2 concentration, as shown in Fig. 7, for experiments performed both in low and high O_2 concentrations. These can be explained from the term of V/A discussed above. Because the PPy film is deposited on the Pd/Nafion electrode with a specified CVD method, the pore volume (V) of the electrode is fixed. However, a higher oxygen concentration implies that oxygen can diffuse more deeply into the PPy-modified
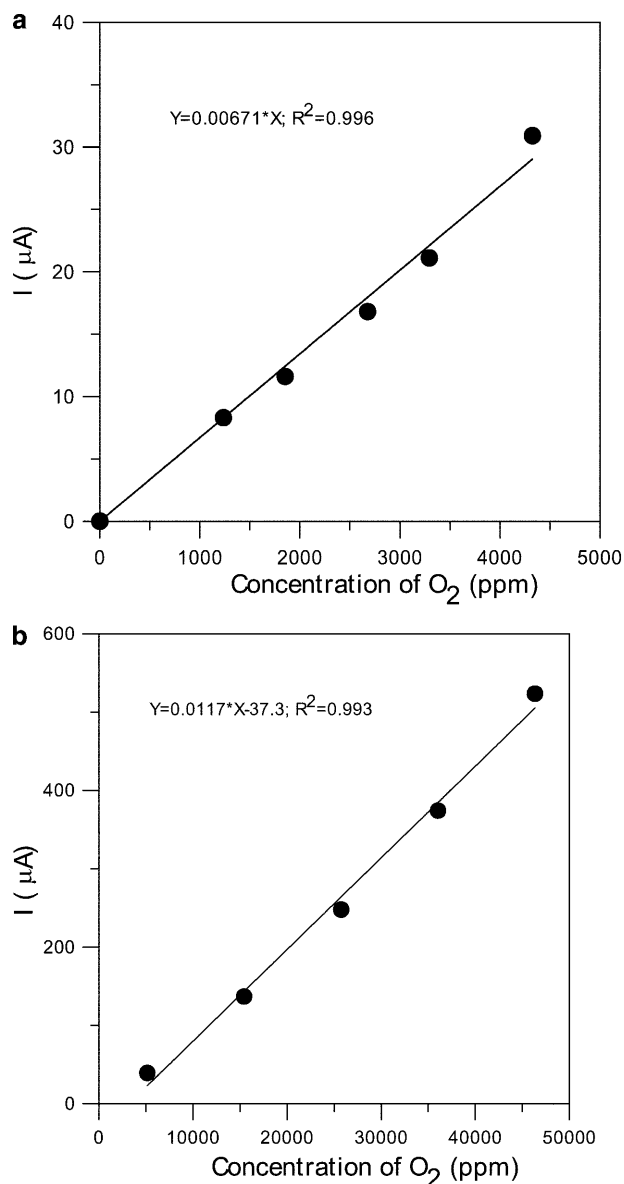
Fig. 5a,b Detected steady current of a PPy-modified Pd/Nafion electrode as a function of oxygen concentrations: **a** 0–5000 ppm; **b** 5000–50,000 ppm

Fig. 6a,b Response time of a PPy-modified Pd/Nafion electrode as a function of oxygen concentrations: **a** 0–5000 ppm; **b** 5000–50,000 ppm

electrode. It results in increasing the available active surface area (A). Thus, a higher oxygen concentration results in a faster steady state reaction, giving shorter response time. On the contrary, there remains a relatively high quantity of unreacted oxygen in the deeper layer in a higher O_2 concentration experiment after the sensed gas is turned off. Therefore, it is difficult to diffuse out from the deeper layer of Nafion film for the remains of oxygen. Thus, a longer recovery time is expected to a steady state in a higher O_2 concentration experiment.

Aging test

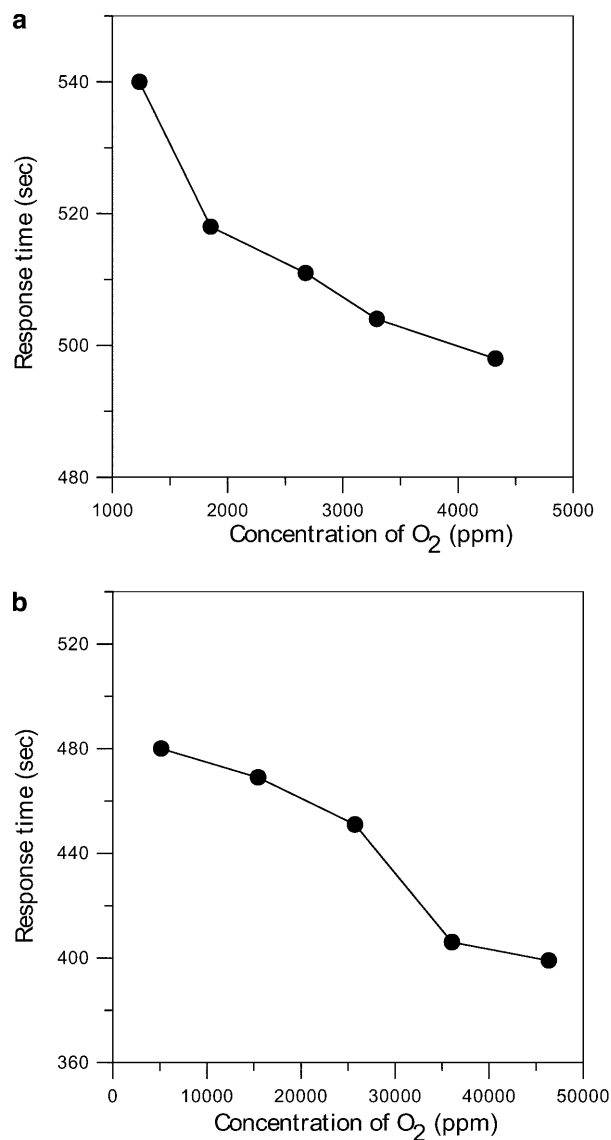Because the catalytic sites of metal on the Pd/Nafion electrode are directly exposed to the sensed gas, the unprotected electrode is aging easily. Thus, the main purpose of the PPy modification is to improve the anti-aging ability in sensing oxygen. Figure 8 demonstrates the sensitivity decay of Pd/Nafion electrodes with and without PPy modification during a sequential oxygen sensing for 48 h. The normalized sensitivity used here is calculated from the ratio of the sensitivity of the electrode during aging to that on the as-prepared electrode. Obviously, the PPy-modified electrode can depress the aging in sensing oxygen. After aging, the sensitivity of the Pt/Nafion electrode without modification demonstrates a serious decrease of 97%. In contrast to this serious decay, an encouraging result shows that the sensitivity of the modified Pd/Nafion electrode just decreases by 53% via a CVD PPy film coated on the electrode.
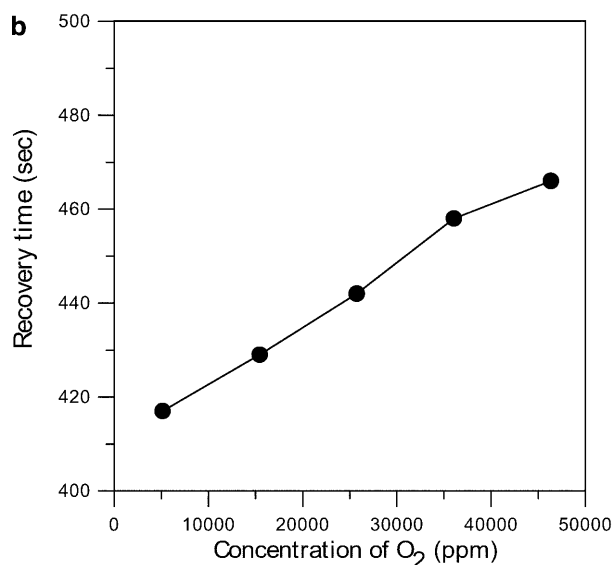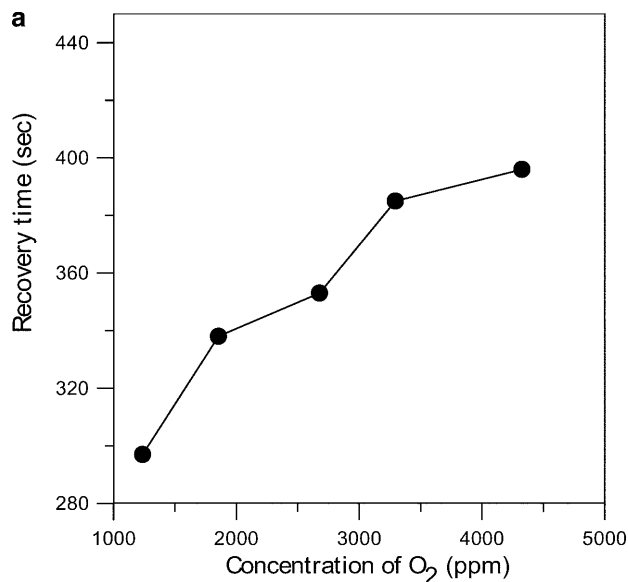
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Fig. 7a,b Recovery time of a PPy-modified Pd/Nafion electrode as a function of oxygen concentrations: **a** 0–5000 ppm; **b** 5000–50,000 ppm
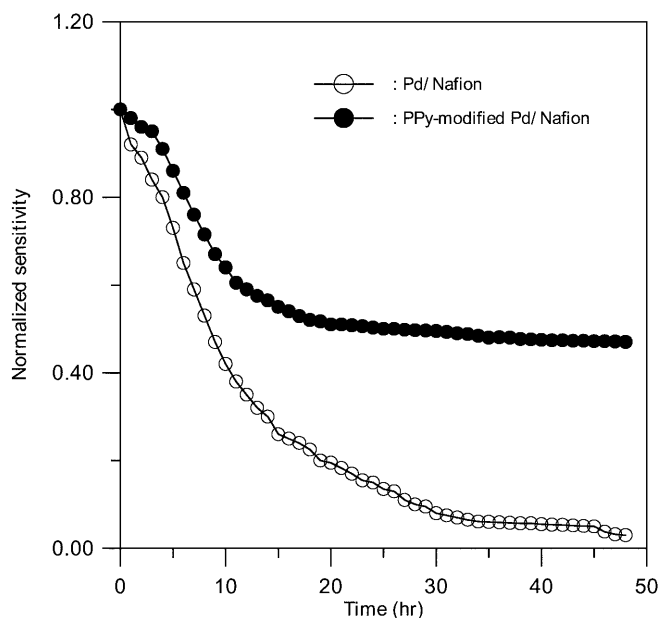

Fig. 8 Variation of the normalized sensitivities of Pd/Nafion electrodes with and without PPy modification with time

97%. In contrast to this serious decay, the sensitivity of the modified Pd/Nafion electrode just decreases by 53% via a CVD PPy film coated on the electrode. Conclusively, the PPy-modified electrode can depress the aging in sensing oxygen.

Conclusion

The Pd/Nafion electrode was prepared by an impregnation-reduction method with a Pd loading of 6.9 mg/cm^2 in sensing oxygen. For improving its anti-aging ability, a polypyrrole (PPy) film was chemically deposited onto the Pd/Nafion electrode. The sensitivities of PPy-modified Pd/Nafion electrodes are 0.00671 and 0.0117 μA/ppm obtained in O_2 concentration regions of 0–5000 and 5000–50,000 ppm, respectively. The response time and the recovery time decreases and increases significantly with increasing O_2 concentrations in both low and high oxygen concentrations. After continuous aging tests for 48 h, the sensitivity of the Pt/Nafion electrode demonstrates a serious decrease of

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