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

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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 O2 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 O2 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.

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/cm². Then the Pd/Nafion was spin-coated with 0.05 mol/l FeCl₃ 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 cm² 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 H₂SO₄, respectively. The various concentrations of oxygen in the O₂-N₂ mixture were determined using a mass-flow-rate controller (Model 840 Mass Meter) and were expressed in ppm (v/v) O₂.

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 (r₁) and by the reduction rate of oxygen (r₂) at active sites within the Pd/Nafion layer, as indicated in Fig. 3. The reaction kinetics can be expressed by

\[ r₁ = kₘ(C_b - C_s) \]  

\[ r₂ = kₙC_s \]  

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