



Electrochemical reduction of NO₂ at a Pt/membrane electrode—Application to amperometric NO₂ sensing

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ABSTRACT

A reductive kinetic study of amperometric NO₂ gas sensing at the Pt/Nafion[®] electrode (or cathode) has been investigated in the concentration range of 0–25 ppm. The Pt/Nafion[®] electrode was prepared using an impregnation–reduction chemical plating method. A Nafion[®] membrane was used as a supporting material and Pt/Nafion[®] sensing electrode as a cathode maintained at a fixed potential of preferably 0.72–0.68 V (vs. Ag/AgCl), which corresponded to the diffusive regions or mass transfer-controlled regions. The SEM photographs showed that the electrode surface with a reductive pretreatment at 0.70 V was porous. By cyclic voltammogram with different scan rates, it was found that the rate of NO₂ reduction was much slower than that of NO₂ oxidation. For NO₂ reduction at the Pt/Nafion[®] cathode fixed in the range of 0.8–0.82 V, transfer coefficient (α), standard apparent rate constant (rk^0) and the exchange current density calculated were 0.32, 9.72×10^{-4} m/s and $19.22 \mu\text{A}/\text{cm}^2$, respectively. The sensing performance, including the long-term stability and the interferences of CO and NO, was also examined.

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1. Introduction

NO₂ gas is a highly toxic gas with a pungent odor, and is harmful to the environment. The maximal tolerable concentration is no greater than 5 ppm for the environmental regulations in many countries. Our previous works [1,2] have shown that NO₂ can be oxidized at the Pt/Nafion[®] electrode (or anode). However, the sensor based on oxidation of NO₂ is significantly affected by interfering NO gas, although less affected by CO gas. The reported sensitivity to NO₂ gas (52 nA/(ppm cm²)) was rather low. In fact, the reduction of NO₂ at different electrodes has also been studied by many researchers [3–10]. The generally accepted mechanism for cathodic reduction of NO₂ involves transfer of two electrons and can be expressed as



Galvanic cell configuration, such as NO₂ (in air)/Pt/neutral buffer halide electrolyte/Ag or active carbon for sensing NO₂ gas, has been fabricated [3–5], although the signal was affected by the presence of O₃ and SO₂ [3]. Hoherčáková and Opekar [6] described a sensing device based on a Au/PVC electrode, at which NO₂ was reduced at –0.5 V (vs. Pt/air electrode). The sensitivity, detection

limit and response time (t_{95}) of this sensor were 400 nA/ppm, 50 ppb and 50 s, respectively. In Roh and Stetter's work [7], NO₂ was reduced at a Au electrode at 0.15 V (vs. Pt/air electrode). The sensitivity and detection limit of the sensing device were 100 nA/ppm and 1.3 ppb, respectively. To improve the selectivity toward ozone, Mizutani et al. [8] proposed a gas diffusion electrode, namely Au/carbon–fluorocarbon membrane, for detection of NO₂ gas. With the attachment of a carbon–fluorocarbon membrane, the interfering effect of ozone can be eliminated. Do and Chang [9] electrodeposited a porous polyaniline layer on a Au/Nafion[®] electrode for improving the sensitivity of the Au/Nafion[®] electrode toward NO₂ gas. Hrnčířová et al. [10] reported that NO₂ can also be reduced at a reticulated vitreous carbon electrode at (–0.5 V vs. Pt/air electrode). The sensitivity, detection limit and response time of this solid-state gas sensor were 277 nA/ppm, 80 ppb and 19 s, respectively.

Another electrochemical reduction technique at elevated temperature (>550 °C) also involves two electrons transfer. According to Miura et al. [11], the reduction reaction that occurs at a Pt/CdCr₂O₄ sensing electrode can be written as



In their work, however, the cathodic current increased exponentially (not to attain stable value) with an incremental cathodic polarization.

Although the sensing characteristics of NO₂ at the Pt, Au, carbon or its composite electrode are reported, the kinetic properties

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of Pt/Nafion[®] electrode sensing system are still not understood. We therefore focus on exploring the kinetic parameters of reducing NO₂ using the Pt/Nafion[®] cathode. The primary objective is to obtain the kinetic parameters for the electroreduction of NO₂ gas at the Pt/Nafion[®] electrode by considering the applied potential in the activation control regime, that is, under small polarization. The kinetic parameters explored include the charge transfer coefficient (α), the standard apparent rate constant (rk^0), and the exchange current density (i_0).

2. Experimental

2.1. Materials, preparation, and sensor configuration of the Pt/Nafion[®] cathode

The Pt/Nafion[®] electrode was prepared using the impregnation–reduction (I–R) procedure. Details on the materials used, the preparation steps, and sensor configuration have been described previously [1,2]. The gas flow rate was controlled by a mass-flow-meter controller (Protec PC-540). N₂ (99.9995%), and standard NO₂ (541 and 27 ppm) in N₂ were purchased from a local gas company (San-Fu Chemical Co., Hsin chu). The 541 ppm NO₂ was used to pretreat the sensing electrode and the 27 ppm NO₂ was used in most sensing experiments.

2.2. Reductive pretreatment of Pt/Nafion[®] electrode

To maintain the electrode/electrolyte interface in an activated state, the Pt/Nafion[®] (sensing) electrode used in this study was activated by repeated potential cycling for the purpose of cleansing. The pretreatment of Pt/Nafion[®] electrode at 0.70 V was similar to that of Pt/Nafion[®] electrode at 1.05 V [1,2]. Similarly, the pretreatment of Pt/Nafion[®] electrode at 0.7 V also included three steps and was conducted at a fixed flow rate of 200 ml/min. Firstly, in order to obtain a steady cathodic current response, a potential of 0.70 V was applied to the sensing electrode in the presence of 500 ppm NO₂ (in N₂ atmosphere) for 3 h. Next, N₂ was passed to the cell containing 0.5 M H₂SO₄ for 1 h to remove the adsorbed NO₂, while the electrode potential was scanned from –0.20 to 1.40 V for 20 cycles at a rate of 20 mV/s using cyclic voltammetry. Finally, the Pt surface of the sensing electrode was cleaned by passing N₂ over it for 3–5 h at 0.70 V.

3. Results and discussion

3.1. The SEM photograph of a reduction pretreated Pt/Nafion[®] electrodes

Fig. 1 is the SEM photograph for the reduction pretreated Pt/Nafion[®] electrode at 0.70 V. It was found that the Pt layer was porous, and the surface of the Pt/Nafion[®] electrode with the reductive pretreatment was rough, as judged by the SEM photograph.

3.2. Cyclic voltammogram (CV) of a Pt/Nafion[®] electrode in N₂ and NO₂

The CVs of a Pt/Nafion[®] electrode, in the presence of N₂ and 25 ppm NO₂ at different scan rates, are shown in Figs. 2–4. It was found that the onset potentials for platinum oxidation and oxygen evolution were approximately at 0.80 and 1.25 V, respectively. The platinum oxide was reduced at potentials between 0.80 and 0.30 V. The onset potential for both NO₂ oxidation and reduction occurring at the Pt surface was found at approximately 0.90 V. In addition, the peak potential for platinum oxide reduction, $E_{p,c}$, shifted to a

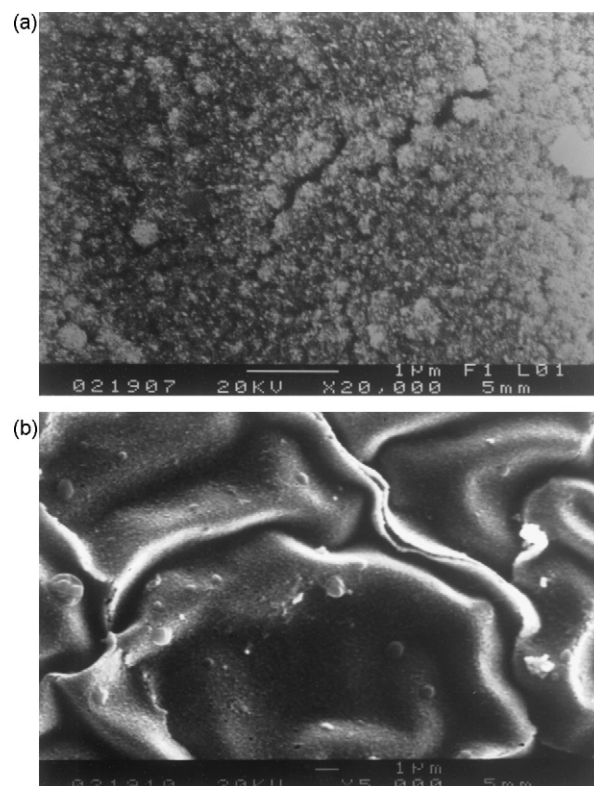


Fig. 1. SEM photographs of a Pt/Nafion[®] electrode after reducing pretreatment at 0.70 V: (a) top view at 20,000 \times ; (b) top view at 5000 \times .

more positive potential as the scan rate was decreased from 0.48 V at a scan rate of 20 mV/s to 0.54 (or 0.58) V at a scan rate of 1 (or 0.25) mV/s. This was probably due to the decreased amount of NO₂ adsorbed on the Pt surface when the scan rate was changed from 20 to 1 (or 0.25) mV/s.

On the other hand, the net peak current densities for NO₂ oxidation (ca. 0.90–1.20 V) were compared with that of NO₂ reduction (ca. 0.80–0.30 V) using various scan rates. At a high scan

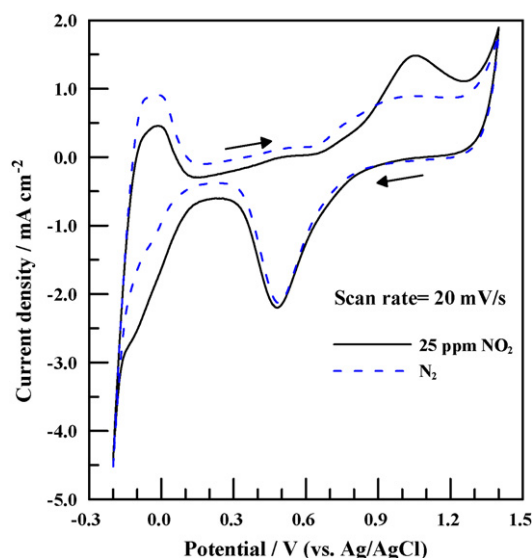


Fig. 2. The potentiodynamic current–potential profiles (or cyclic voltammograms) for a Pt/Nafion[®] electrode run at 20 mV/s. Gas phase: (—) 25 ppm NO₂; (---) pure N₂; solution: 0.5 M H₂SO₄; gas flow rate is 200 ml/min.

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