A kinetic study for electrooxidation of NO gas at a Pt/membrane electrode-application to amperometric NO sensor

Kuo-Chuan Ho^{a,b,*}, Jung-Yu Liao^a, Chin-Cheng Yang^a

^a Department of Chemical Engineering, National Taiwan University, Taipei 10617, Taiwan

^b Institute of Polymer Science and Engineering, National Taiwan University, Taipei 10617, Taiwan

Received 13 July 2004; received in revised form 14 December 2004; accepted 27 December 2004

Available online 3 March 2005

Abstract

The electrochemical oxidation of nitric oxide (NO) gas at a Pt/membrane electrode has been studied. The Pt/Nafion® electrode was prepared by the impregnation–reduction (I–R) chemical plating method and was tested over the NO concentration range from 0 to 500 ppm. It is assumed that the electrooxidation of NO gas at the electrode can be considered as an irreversible process, from which a transcendental equation describing the I – E relationship can be derived. The derived I – E relationship fits the experimental data reasonably well. Several electrochemical parameters for the reaction, including the half-wave potential ($E_{1/2}$), the standard apparent rate constant (ra_k^0), the transfer coefficient (α), and the exchange current density (i_0) can be extracted from the experimental data. Under the kinetic controlled regime, with the potential in the range of 0.7–0.9 V (versus Ag/AgCl/sat. KCl), the kinetic model predicts the electrooxidative behavior of NO at a Pt/Nafion® electrode over a wide concentration range of 100–500 ppm. An amperometric NO gas sensor based on a Pt/Nafion® electrode has been fabricated and tested over the NO concentration range from 0 to 500 ppm at 1.15 V (versus Ag/AgCl/sat. KCl) and a flow rate of 200 ml per min.

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Keywords: Amperometric sensor; Kinetic study; Nitric oxide (NO); Pt/Nafion® electrode; Sensitivity

1. Introduction

Nitric oxide (NO) gas, formed during combustion processes in power plants, waste incinerators and combustion engines such as automobiles, is among the major air pollutants leading to the formation of photochemical smog and acid rain. Therefore, the development of a NO sensor is a very important task from the environmental protection point of view. Although monitoring of NO gas concentrations has been accomplished, for decades, by monitoring a conductivity change in SnO₂-based sensors commercially available, their high temperature and long response time make SnO₂ undesirable for some applications. A highly selective, sensitive, and stable NO sensor remains to be developed [1].

A variety of techniques have been developed for the purpose of detecting NO gas concentration with a lower limit. The detection methods include chemiluminescence, photoluminescence, thermal conductivity, semiconductor electrical conductivity, electrochemistry, etc. The advantages of the electrochemical method are quicker response and lower cost compared to the other methods. Three types of NO gas sensors have been developed based on the electrochemical technique, namely, amperometric sensors [2–9], potentiometric sensors [10–15], and semiconductor-type sensors [16–20]. Among the amperometric sensors, both electrooxidation and electroreduction have been employed for the detection of NO gas. Mostly, it is based on electrochemical oxidation, at both room temperature [2–7] and high temperature [8]; with only a few based on electrochemical reduction [9]. Table 1 summarizes the operating condition (e. g., potential and/or temperature) and output signal of the NO concentration studied in the gas phase at various noble sensing metals.

* Corresponding author. Tel.: +886 2 2366 0739; fax: +886 2 2362 3040.
 E-mail address: kcho@ntu.edu.tw (K.-C. Ho).

Table 1

The operating condition and output signal for sensing NO concentration in the gas phase studied at various electrodes

Sensing electrodes	Operating condition	Output signal	Ref.
Metal/membrane ^a	0.96–1.03 V vs. SHE	Current	[2]
Au/Teflon [®]	1.5 V vs. SHE	Current	[3]
Au/hydrophobic plastic ^b	1.6 V vs. SHE	Current	[4,5]
Au/C	0.9–1.5 V vs. SHE	Current	[6]
Au/Nafion [®]	0.7 V vs. MSE ^c	Current	[7]
Pt/Nafion [®]	0.7 V vs. MSE ^c	Current	[7]
Pt/Nafion [®]	1.15 V vs. sat. Ag/AgCl	Current	This work

^a Sensing material is mainly Au/Teflon[®]. Noble metal: e.g., Pt, Pd, Ir, and the like; membrane: e.g., polyethylene (PE), polypropylene (PP), and the like.

^b Sensing material is mainly Au/Teflon[®]. Hydrophobic plastic: e.g., polyacrylonitrile, polyvinyl chloride, polyvinyl alcohol, and carboxymethyl cellulose, or the like.

^c A saturated mercury-mercurous sulfate electrode (MSE, $E = 0.64$ V vs. SHE).

Chand [2] reported that NO electrooxidation occurred between 0.96 and 1.03 V (versus SHE) at a metal/membrane electrode with an acidic electrolyte. Sedlak and Blurton [3–6] also oxidized NO at 1.5, 1.6, and 0.9–1.5 V (versus SHE) on Au/Teflon[®], Au/hydrophobic plastic, and Au/C electrodes, respectively. They obtained a current plateau when potential was larger than 1.2 V (versus SHE) [3]. The reported current density was $7.8 \mu\text{A}/\text{cm}^2$ at a Au electrode. According to Jacquinot et al. [7], NO could be oxidized at Pt/Nafion[®] and Au/Nafion[®] electrodes at 0.70 V versus MSE (mercury-mercurous sulfate electrode) using 10 M H₂SO₄ electrolyte solution passing 0–1 ppm NO. The sensitivities of NO₂ and NO gases were 550 nA/ppm (or 696 nA/ppm/cm²) and 203 nA/ppm (or 257 nA/ppm/cm²), respectively, at the same Pt/Nafion[®] electrode. The cross-sensitivity of NO₂ with respect to NO was found to be 2.7. This NO gas sensor was significantly affected by interfering NO₂ gas in the 0–1 ppm range.

It is generally accepted that the main electrochemical oxidation at the Au or Pt or other noble metals [2–9] involves transfer of three electrons and can be expressed as

Although NO can be oxidized at the Au or its composite electrodes, both the electrooxidation of NO and its amperometric responses on the Pt/Nafion[®] electrode are less studied. In this study, a repetitive potential scanning procedure was adopted to ensure the cleanliness of the electrode/electrolyte interface. By properly activating the Pt/Nafion[®] electrode, the electrooxidation of NO gas was carried out under potentiostatic conditions and the data were analyzed to obtain the kinetic parameters. According to Jacquinot et al. [7], the NO sensor was significantly affected by interfering NO₂ gas at the Pt/Nafion[®] electrode. We therefore aimed in this study to increase the sensitivity of NO and to decrease the NO₂ interference by adopting a proper activating procedure for the Pt/Nafion[®] electrode. The sensing characteristics of NO ox-

idation at the Pt/Nafion[®] interface, including the operating potential, sensitivity, and interfering gases (NO₂ and CO), were studied in the high concentration range of 0–500 ppm.

In our previous work [21], we have shown that NO gas can be oxidized at the Pt/Nafion[®] electrode. The values of the charge transfer coefficient and the exchange current density can thus be obtained by fitting the experimental rate data with the Tafel equation. However, this becomes plausible only when the applied potential is large enough. In this study, we will study the electrooxidation of NO 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 (r_{ak}^0), the half-wave potential ($E_{1/2}$), and the exchange current density (i_0).

2. Experimental

2.1. Sensing electrode-preparation and characterization

The Pt/Nafion[®] electrode was prepared by the impregnation–reduction procedure. The platinum loading was controlled at $2 \text{ mg}/\text{cm}^2$. Details on the preparation of the Pt/Nafion[®] electrode, as well as the configuration of the sensor system, have been described previously [21,22]. N₂ (99.9995%), standard NO gas (500 ppm) in N₂, standard NO₂ gas (541 ppm) in N₂, and standard CO gas (513 ppm) in N₂, were purchased from a local gas company (San-Fu Gas Co., Hsin-Chu). All chemicals used in this work were reagent grade and were used as received. Deionized water (DIW) was used throughout this work. All electrochemical measurements were performed at room temperature in a three-electrode configuration cell, with a Ag/AgCl/sat. KCl as the reference electrode. An EG&G (Model 273A) potentiostat/galvanostat was used to control the potential applied to the working electrode. The geometric area of the sensing electrode was 3.14 cm^2 .

2.2. Pretreating Pt/Nafion[®] electrode by cyclic voltammetric (CV) activation

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. This was done in a cell containing 0.5 M H₂SO₄ by scanning the electrode potentials between -0.2 and 1.4 V for 10 cycles at a scan rate of $20 \text{ mV}/\text{s}$ under N₂ at a flow rate of $200 \text{ ml}/\text{min}$. The intention of the repetitive scanning was to clean or remove adsorbed gases (NO, NO₂ or CO) by passing N₂. In fact, the open-circuit potential can be used as an indicator for the cleanliness of the electrode/electrolyte interface. Right after the cleaning, additional 30 min to 1 h was needed for the electrode to reach a steady-state open-circuit potential, or the equilibrium

potential. The open-circuit potential was measured immediately after the activation procedure. The whole cleaning process thus can be followed by monitoring the drift of the open-circuit potential. Except for the fresh electrode, the experimental data reported below with the Pt/Nafion[®] electrodes were all pretreated before each sensing experiment.

2.3. Determination of real surface area

The real surface area of the Pt/Nafion[®] electrode was determined from the charge of oxidation in the adsorbed hydrogen region (by integrating the stationary cyclic voltammogram) after subtracting the double-layer charge. The conversion factor of 210 $\mu\text{C}/\text{real cm}^2$ for Pt was used as the saturation coverage [23–26]. The voltage was scanned from -0.2 to 1.4 V (versus Ag/AgCl) at a scan rate of 20 mV/s. The same cell was used to obtain the nitric oxide oxidation polarization.

3. Theoretical consideration

When nitric oxide (NO) was introduced into the detection (gas) chamber, it was rapidly oxidized to nitrate. The electrochemical oxidation of nitric oxide at the working electrode involves three electrons per mole of NO as described by the above Eq. (1). The rate equation for the consumption of NO can be written as:

$$R_{\text{NO}} = \frac{I}{nF} = AarkC_s \quad (2)$$

where a is the ratio of the active surface area to the real surface area, or called the fractional active area, r is the ratio of the real surface area to the geometrical area, or called the roughness factor. The other symbols have their usual meanings, that is, I , n , F , A , k , and C_s represent the current, the number of transferred electrons, the Faraday constant, the geometric area, the rate constant and the surface concentration of NO at the active surface, respectively. The apparent rate constant, ark , can be related to the electrode potential according to the following equation [27]:

$$ark = ark^0 \exp[(1 - \alpha)nf(E - E^0)] \quad (3)$$

where $f = F/RT$, α , k^0 , and E^0 are the transfer coefficient, the standard rate constant, and the formal potential, respectively. Logarithm of Eq. (3) gives

$$\ln(ark) = [\ln(ark^0) - (1 - \alpha)nfE^0] + (1 - \alpha)nfE \quad (4)$$

A plot of $\ln(ark)$ against the electrode potential E gives a slope of $(1 - \alpha)nf$, from which the charge transfer coefficient, α , can be obtained.

A microscopic model is considered here to distinguish the heterogeneous nature at the gas/membrane electrode interface. A schematic on the surface of a membrane electrode corresponds to this model is shown in Fig. 1. Two platinum sites, active and non-active, are proposed. Active sites refer to the Pt sites where the NO oxidation takes place. Non-active

Fig. 1. A microscopic model showing the active and non-active sites on the surface of a Pt/membrane electrode.

sites represent the sites without electro-activity with respect to the NO oxidation. Let C_s and C_b be the concentrations of NO in the vicinity of active sites and non-active sites, respectively. Considering a differential thickness d over the surface of Pt sites, a mass balance of NO on the differential volume, with a thickness d and a real surface area of A_r , containing an averaged concentration $\bar{C}_s$, gives

$$Ard\bar{C}_s = AardC_s + A_r(1 - a)dC_b \quad (5)$$

or,

$$\bar{C}_s = aC_s + (1 - a)C_b \quad (6)$$

At steady-state, the rate of consumption of NO by the reaction is equal to the rate of supply of NO by the diffusion,

$$R_{\text{NO}} = AarkC_s = A \frac{D}{L} (C_b - \bar{C}_s) \quad (7)$$

Substituting Eq. (6) into Eq. (7) yields

$$R_{\text{NO}} = AarkC_s = Aa \frac{D}{L} (C_b - C_s) \quad (8)$$

Thus, the concentrations of NO in the vicinity of active sites, C_s , can be expressed in terms of the bulk concentration, C_b . The result is

$$C_s = \frac{D}{L} \frac{1}{(D/L) + rk} C_b \quad (9)$$

Substituting Eq. (9) into Eqs. (2) and (3) gives,

$$\begin{aligned} R_{\text{NO}} &= \frac{I}{nF} = \frac{1}{1/((D/L) + (1/rk))} AaC_b \\ &= \frac{1}{1/(D/L) + 1/rk^0 e^{(1-\alpha)nf(E-E^0)}} AaC_b \end{aligned} \quad (10)$$

This equation relates the electrooxidation current to E and other parameters, such as the formal potential, the charge transfer coefficient, and the standard rate constant.

Case I: when $rk^0 \exp[(1 - \alpha)nf(E - E^0)] \ll D/L$, or the kinetic-control regime: Eq. (10) becomes

$$I = nFAark^0 \exp[(1 - \alpha)nf(E - E^0)]C_b \quad (11)$$

At equilibrium, $E = E_{eq} \approx E^0$, the exchange current density can be written as

$$i_0 = nFark^0 C_b \quad (12)$$

Case II: when $rk^0 \exp[(1 - \alpha)nf(E - E^0)] \gg D/L$, or the mass-transfer control regime, Eq. (10) becomes

$$I_l = nFAa \frac{D}{L} C_b \quad (13)$$

4. Results and discussions

4.1. Real surface area of a fresh Pt/Nafion® electrode

Typical cyclic voltammogram (CV) of the fresh Pt/Nafion® electrode, in contact with 0.5 M H₂SO₄ solution in N₂ atmosphere at a flow rate of 200 ml/min, is shown in Fig. 2. The potential was scanned from −0.2 to 1.4 V at a scan rate of 20 mV/s. The peaks are designated in their order of appearance with increasing anodic potential as “O_{A1}”, “O_{A2}”, and “O_{A3}”, continuing into O₂ evolution process. H adsorption and ionization peaks “H_A”, “H_C”, etc., at more cathodic potentials are also indicated together with the cathodic region “O_C” for surface oxide reduction. The cathodic and anodic peaks at $E < 0.2$ V (versus Ag/AgCl/sat. KCl) are respectively due to the electrochemical adsorption and desorption of hydrogen on the Pt/Nafion® electrode. The anodic peaks at $E > 0.6$ V are ascribed to the surface oxide formation and the cathodic peak at $E \approx 0.43$ V is ascribed to the surface oxide reduction. For example, the oxidation peak at O_{A2} (Fig. 2) is ascribed to the following reaction [28]:

Fig. 2. Typical CV for a Pt/Nafion® electrode scanned in pure N₂ at 20 mV/s. The electrolyte is 0.5 M H₂SO₄. The gas flow rate is maintained at 200 ml/min.

where Pt–O represents a layer of adsorbed oxygen atoms on the Pt surface. This Pt/Pt–O reaction favored the operating potential range (0.75–1.00 V) at the Pt electrode. Beyond 1.00 V, a layer of oxide, PtO, was formed. The evolutions of hydrogen and oxygen take place at about $E < -0.2$ V and $E > 1.25$ V, respectively. The electrochemical active surface area of platinum was determined from the integration of the charge of oxidation in the adsorbed hydrogen region of the stationary CV after subtracting the double layer charge and use 210 $\mu\text{C}/\text{real cm}^2$ as the saturation coverage [23–26]. The charge under Area I in Fig. 2, or the charge of the desorbed hydrogen, was measured to be 8.10 mC/cm², hence the roughness factor (real area/geometric area) for the Pt/Nafion® electrode would be 38.6 real cm²/cm² of the geometrical area.

4.2. Kinetic parameters

To obtain the kinetic parameters for the reaction, the applied potential was controlled in the kinetic region. In this case, the surface concentration of NO is very close to the bulk concentration, i.e., $C_s \approx C_b$. From Eq. (2), the fundamental electrokinetic equation for an irreversible reaction can be written as

$$\frac{I}{A} = nFrakC_b = nFrak^0 \exp[(1 - \alpha)nf(E - E^0)] \quad (15)$$

Taking natural logarithm for Eq. (15), one obtains

$$\ln \left[\frac{I}{A} \right] = \ln[nFrak] + \ln[C_b] = y_0 + \ln[C_b] \quad (16)$$

where $y_0 = \ln[nFrak]$. According to Eq. (16), a plot of $\ln[I/A]$ versus $\ln[C_b]$ gives an intercept (y_0) which is equal to $\ln[nFrak]$. Fig. 3 shows the plots of $\ln[I/A]$ versus $\ln[C_b]$ in

Fig. 3. A plot of $\ln[I/A]$ vs. $\ln[C_b]$ for NO electrooxidized a Pt/Nafion® electrode at different applied potentials. The electrolyte is 0.5 M H₂SO₄. The gas flow rate is maintained at 200 ml/min.

the kinetic control regime of 0.80, 0.85, and 0.90 V by using the same Pt/Nafion[®] electrode. It was found that the slopes were very close 1.0 for all three potentials, as required by Eq. (16). The following equation can be used to convert from one basic unit (ex, A/m² and mole/m³) to another unit (ex, $\mu\text{A}/\text{cm}^2$ and ppm):

$$\ln \left[\frac{I}{A} (\mu\text{A}/\text{cm}^2) \times 10^{-2} (\text{A}/\text{m}^2) / (\mu\text{A}/\text{cm}^2) \right] \\ = \ln[nF\text{rak}] + \ln[C_b(\text{ppm}) \times 4.1 \times 10^{-5} \text{ mol}/\text{m}^3 \text{ ppm}]$$

or,

$$\ln \left[\frac{I}{A} (\mu\text{A}/\text{cm}^2) \right] = \ln(3 \times 96,487 \times (4.1 \times 10^{-3}) \times \text{rak}) \\ + \ln[C_b(\text{ppm})]$$

and,

$$\text{rak} = 8.44 \times 10^{-4} \exp(y_0) \quad (17)$$

The concentration unit, converting from ppm to mol/m³, can be done by the following equation

$$C_{\text{total}} = \frac{n_t}{V} = \frac{P}{RT} \\ = \frac{1 \text{ atm}}{(0.082 \text{ atm l/mol K}) \times 298 \text{ K}} \times 10^3 \text{ l}/\text{m}^3 \\ = 41.0 \text{ mol}/\text{m}^3, \quad C_b = 4.1 \times 10^{-5} \text{ mol}/(\text{m}^3 \text{ ppm})$$

According to Eq. (17), the apparent rate constant, *rak*, can be obtained from the intercept (*y*₀) in a plot of $\ln[I/A]$ versus $\ln[C_b]$, as indicated by Eq. (16). Table 2 summarizes the values of the intercept, the slope, and the corresponding apparent rate constant at various applied potentials.

Fig. 4 shows a plot of $\ln(\text{rak})$ versus *E* at a Pt/Nafion[®] electrode. The transfer coefficient (α) was calculated to be 0.81 from the slope (22.47 V⁻¹). The intercept (*y*₀^{*}) was -26.84 (m/s) and is related to the standard apparent rate constant and the formal potential according to Eq. (4)

$$y_0^* = \ln(\text{rak}^0) - (1 - \alpha)nfE^0 \quad (18)$$

The formal potential (*E*⁰) is close to the open circuit potential which was measured experimentally with a value of 0.75 V. Therefore, the apparent standard rate constant (*ark*⁰) and the exchange current density (*i*₀) were calculated to be 4.58×10^{-4} m/s and $27.2 \mu\text{A}/\text{cm}^2$, respectively. The current densities collected in the kinetic control region follows an

Table 2

The value of the apparent rate constant as a function of the applied potential (the intercept and the slope of Fig. 3 are also shown)

<i>E</i> (mV) vs. Ag/AgCl	Intercept, <i>y</i> ₀	Slope	<i>rak</i> (m/s)
800	-1.937	0.985	1.217×10^{-4}
850	-0.373	0.976	5.812×10^{-4}
900	0.310	0.971	1.151×10^{-3}

Fig. 4. A plot of $\ln[\text{rak}]$ vs. *E* for NO electrooxidation on a Pt/Nafion[®] electrode. The electrolyte is 0.5 M H₂SO₄. The gas flow rate is maintained at 200 ml/min.

empirical equation, from which the kinetic parameters for the reaction were extracted.

4.3. Effect of sensing potential-polarization data

The steady-state polarization data, or the net current density (*i*) versus potential (*E*) plot for the oxidation of 500 ppm NO gas at the Pt/Nafion[®] electrode, are shown in Fig. 5. At each potential level, the procedure began with stepping the potential from the open-circuit potential (0.75 V) to the chosen potential under 500 ppm NO in N₂, followed by a CV activation process. Then a background current density at the same potential level was obtained in N₂ purge. Finally, this run was ended with a final CV activation. The complete polarization data were obtained by repeating the procedure

Fig. 5. The net limiting current density-potential (*I-E*) data for oxidizing 500 ppm NO at a Pt/Nafion[®] electrode. The gas flow rate is maintained at 200 ml/min. The solid line is obtained by fitting Eq. (19) with *i*_{l,a} = 930 $\mu\text{A}/\text{cm}^2$, *E*_{1/2} = 0.88 V, and $\alpha = 0.81$.

mentioned above. The potentials of the Pt/Nafion[®] electrode were increased sequentially from 0.35 to 1.30 V. The net current density increased to 980 $\mu\text{A}/\text{cm}^2$ as the operating potential was increased to 1.0 V. The zero net current density was experimentally observed at 0.75 V, which corresponds to the equilibrium potential (E_{eq}) for the oxidation reaction. For an irreversible reaction, the polarization data over a wide potential range, including both kinetic and mass transfer controlled regions, can be expressed by the following transcendental equation [29]:

$$\frac{i}{i_{\text{L,a}}} = \frac{1}{1 + e^{-(1-\alpha)nF(E-E_{1/2})/RT}} \quad (19)$$

where $i_{\text{L,a}}$ is the anodic limiting current density, $E_{1/2}$ is called the half-wave potential; that is, $E = E_{1/2}$ when $i = i_{\text{L,a}}/2$. It can be shown by a semi-empirical treatment of steady-state mass transfer that $E_{1/2} \approx E^0$, if the reactant and the product species have similar values of mass transfer coefficient. In this case, Eq. (19) is the same as Eq. (10). The smooth curve in Fig. 5 is obtained by plotting Eq. (19) with $i_{\text{L,a}} = 930 \mu\text{A}/\text{cm}^2$, $E_{1/2} = 0.88 \text{ V}$, and $\alpha = 0.81$. For the NO oxidation reaction taking place in the kinetic controlled region, the potential at the Pt/Nafion[®] electrode should be controlled between 0.75 and 0.90 V; while to ensure the operation in the diffusive or mass transfer controlled region, the Pt/Nafion[®] electrode is preferably operated in the potential range of 1.0–1.2 V.

4.4. Sensitivity and interferences

Fig. 6 shows the current density versus time transients of the NO sensor in response to a potential step change from the open circuit potential (0.75 V) to 1.15 V at various NO concentrations. It can be seen from Fig. 6 that the steady limiting currents have been reached for all concentrations investigated. Fig. 7 shows the net current densities versus

Fig. 6. The current density vs. time transients for NO electrooxidation in response to a potential step change from 0.75 to 1.15 V at various NO concentrations.

Fig. 7. The net limiting current density dependence of NO, NO₂, and CO concentrations (0–500 ppm) at the same sensing electrode, showing the low cross-sensitivities of interfering gases NO₂, and CO with respect to NO gas.

concentrations of NO, NO₂, and CO in the range from 0 to 500 ppm at the same Pt/Nafion[®] sensing electrode. The same procedure has been applied to all gases investigated. The anodic steady currents were obtained by stepping the potential from the open circuit value of 0.75–1.15 V and a fixed flow rate of 200 ml/min. When passing NO, NO₂, and CO gases, the sensing responses were linear for all three gases in the concentration range of 0–500 ppm. According to Fig. 7, the sensitivities (0–500 ppm) were calculated to be 1.42 $\mu\text{A}/\text{ppm}/\text{cm}^2$, 0.1 $\mu\text{A}/\text{ppm}/\text{cm}^2$, and 0 $\mu\text{A}/\text{ppm}/\text{cm}^2$ at the same Pt/Nafion[®] electrode for NO, NO₂ and CO, respectively. The sensitivity (1.42 $\mu\text{A}/\text{ppm}/\text{cm}^2$) was about 5.5 times higher than that (0.26 $\mu\text{A}/\text{ppm}/\text{cm}^2$) of Jacquinot et al. [7] reported at the Pt/Nafion[®] electrode for sensing NO. Since Pt started to oxidize at 0.75 V and became fully oxidized beyond 1.00 V, as mentioned earlier in Section 4.1, it was inferred that the Pt–O surface was sensitive to NO, but not CO, based on Fig. 7. This finding was consistent with an observation made by Tsceng and Yang [30], who pointed out that platinum became insensitive to CO due to PtO formation when the sensing potential was more positive than 1.0 V. The cross-sensitivities (sensitivity of interfering gas/sensitivity of NO) for NO₂ and CO in the 0–500 ppm range were found to be around 0.07 and 0, respectively. Therefore, by stepping the potential from the open circuit value up to 1.15 V, this sensor was only slightly affected by NO₂ gas, but was hardly affected by CO gas. The cross-sensitivities found in this study in the range 0–500 ppm was smaller than those reported in the literature in the range 0–1 ppm [7].

5. Conclusions

This work reported the kinetic study of NO gas at the Pt/Nafion[®] electrode with application to the amperometric

NO sensing based on the same electrode. The electrooxidation reaction of NO on the Pt/Nafion[®] electrode was examined over a wide potential range of 0.35–1.30 V (versus Ag/AgCl/sat. KCl) and over a wide concentration range of 0–500 ppm. When the applied potential is small enough, the electrooxidation reaction is activation control. The experimental data fitted well with a fundamental electrokinetic equation for an irreversible reaction, from which the standard apparent rate constant (ra_k^0) and the transfer coefficient (α) of the reaction were found to be 4.58×10^{-5} m/s and 0.81, respectively. The exchange current density for the electrooxidation of NO gas on the Pt/Nafion[®] electrode was calculated to be $27.2 \mu\text{A}/\text{cm}^2$. For the amperometric sensor application, the applied potential of the Pt/Nafion[®] electrode was chosen in the diffusive region (or the mass transfer controlled region) of preferably 1.15 V (versus Ag/AgCl/sat. KCl). The NO was oxidized at the Pt/Nafion[®] electrode at room temperature by stepping the potential from the open circuit value of 0.75–1.15 V. The sensitivity of the NO sensor was found to be $1.42 \mu\text{A}/\text{ppm}/\text{cm}^2$ for a fixed flow rate of 200 ml/min. The sensitivity of NO on the Pt/Nafion[®] electrode was 5.5 times higher than that reported in literature. Presumably, this is due to the CV activation procedure that increases the active sites for NO oxidation. The cross-sensitivities of NO₂ and CO were found to be 0.07 and 0, respectively.

Acknowledgement

This research was supported by the Program for Promoting Academic Excellence of Universities, sponsored by the Ministry of Education of the Republic of China, under grant number EX-91-E-FA09-5-4.

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Biographies

Kuo-Chuan Ho received BS and MS degrees in Chemical Engineering from National Cheng Kung University, Tainan, Taiwan, in 1978 and 1980, respectively. In 1986, he received the PhD degree in chemical engineering at the University of Rochester. The same year he joined PPG Industries, Inc., first as a Senior Research Engineer and then, from 1990 until 1993, as a Research Project Engineer. He has worked on the electrochemical properties of various electrode materials, with emphasis on improving the performances of sensor devices. Following a 6-year industrial career at PPG Industries, Inc., he joined his alma mater at National Cheng Kung University in 1993 as an associate professor in the Chemical Engineering Department. In 1994, he moved to the Department of Chemical Engineering at National Taiwan University. Currently, he is a Professor jointly appointed by the Department of Chemical Engineering and Institute of Polymer Science and Engineering at National Taiwan University.

Jung-Yu Liao received his BS degree in Chemical Engineering from National Taiwan University, Taipei, Taiwan, in 1999. He received PhD degree in chemical engineering from National Taiwan University in 2004. Currently, he is in the army to fulfill the compulsory military service. His research interest mainly surrounds applications of chemically modified electrodes on sensing and electro-optical devices.

Chin-Cheng Yang received his BS degree in Chemical Engineering from National Taiwan University, Taipei, Taiwan, in 1995. He received MS degree in chemical engineering from National Taiwan University in 1997. Currently, he is a Manager in Photo Process Development Department at Macronix International Co., Hsinchu, Taiwan. His research interest mainly is focused on the electrochemical gas sensors and the new/next generation litho development for flash memory applications.