ELSEVIER

Sensors and Actuators B 79 (2001) 11–16

SENSORS AND ACTUATORS B CHEMICAL

www.elsevier.com/locate/sensorb

An amperometric NO_2 gas sensor based on Pt/Nafion® Electrode

Kuo-Chuan Ho*, Wen-Tung Hung

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

Received 27 November 2000; received in revised form 10 March 2001; accepted 22 March 2001

Abstract

An amperometric NO_2 gas sensor based on Pt/Nafion® electrode has been prepared using an impregnation–reduction chemical plating method and tested over the NO_2 concentration range from 0 to 485 ppm. A Nafion® membrane was used as a supporting material and Pt/Nafion® electrode as an anode maintained at a fixed potential, diffusive regions (or mass transfer controlled regions) with respect to a reference electrode of preferably 0.95–1.10 V. A 45 s response time (t_{95}) was attained with a 0–485 ppm step change in NO_2 concentration whereas the recovery time (t_{95}) was 54 s when the NO_2 concentration was stepped from 485 to 0 ppm. The sensitivity for the NO_2 (0–100 ppm) gas sensor was 0.16 μA/ppm (52 nA/ppm/cm^2) at room temperature. The NO_2 sensor, based on a Pt/Nafion® electrode, showed a long-term stability greater than 27 days, suggesting its possible applicability for environmental monitoring. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Amperometric sensor; Nitrogen dioxide (NO_2); Pt/Nafion® electrode; Recovery time (t_{95}); Response time (t_{95}); Sensitivity

1. Introduction

Nitrogen dioxide (NO_2), an environmental pollutant, is an extremely toxic gas and causes photochemical smog and acid rain which deteriorates our environment. Therefore, the development of an NO_2 sensor is a very important task from the environmental protection point of view.

The NO_2 concentration is generally measured by chemiluminescene [1,2] and electrochemical methods [3–17]. The electrochemical method uses two types of sensors, i.e. the amperometric sensor [3–14] and the potentiometric sensor [14–17]. The electrochemical method, in general, shows rapid response time and lower cost than the chemiluminescene method. Amperometric sensors, in particular, exhibit higher sensitivity and selectivity for NO_2 gas than potentiometric sensors. There are many supporting materials available for developing gas sensors. These include Teflon (PTFE), polyacrylonitrile (PAN), polyethylene (PE), polypropylene (PP), polyvinyl chloride (PVC), carboxymethyl cellulose, and carbon etc. Nafion® membrane, a perfluorinated cation exchange membrane, is a copolymer of tetrafluoroethylene and sulfonyl fluoride vinyl ether, has been widely used due to its high ionic conductivity, excellent perm-selectivity and good mechanical strength.

A sensing electrode, usually made of inert metallic materials, is used along with supporting membranes to assemble an amperometric NO_2 sensor. They may be noble metal/membrane [3], Au/hydrophobic plastic [4,5], Au/Nafion® [6,7], Au/C/Nafion® [8], Au/Teflon [9–11], Au/C [12], Au [13] and Pt/$CdCr_2O_4$ [14] just to name a few. The electroanalytical procedures employed for NO_2 detection are mostly based on two types of electrochemical reduction [5–13,14] with a few based on its electrochemical oxidation [3,4]. The main electrochemical reduction [5–13] at the sensing electrode can be expressed as

$$NO_2 + 2H^+ + 2e^- \rightarrow NO + H_2O \quad (1)$$

Another electrochemical reduction [14] at the sensing electrode can be expressed as

$$NO_2 + 2e^- \rightarrow NO + O^{2-} \quad (2)$$

The electrochemical oxidation reaction [3] at the sensing electrode can be expressed as

$$NO_2 + H_2O \rightarrow HNO_3 + H^+ + e^- \quad (3)$$

According to Chand [3], NO_2 can be oxidized at the sensing electrode (noble metal/membrane) at 0.8 V versus a standard hydrogen electrode (SHE). The noble metals used are Au, Pt, Pd, Ir whereas the membrane can be made of Teflon, PE, PP. Blurton and Sedlak [4] also reported oxidized current at 1.6 V versus SHE for NO_2 sensing with an

---

* Corresponding author. Fax: +886-2-2362-3040.
E-mail address: kcho@ms.cc.ntu.edu.tw (K.-C. Ho).

PII: S0925-4005(01)00782-1

Au/hydrophobic-plastic electrode. However, the electrochemical properties of NO_2 gas sensors based on Pt/Nafion® electrode or Pt electrode are still unconfirmed. We aim in this paper to show how NO_2 can be oxidized at a Pt/Nafion® electrode. Only a few electrochemical studies on oxidizing NO_2 exist in the open literature which motivated our efforts to make an amperometric NO_2 gas sensor.

2. Experimental

2.1. Materials

Perfluorosulfonic acid polymer sheets as Nafion® 117 (Dupont de Nemours) were used as a supporting membrane (equivalent weight 1100 and dry thickness 178 μm). Methanol (CH_3OH, 99.99%), H_2O_2 (35%), H_2SO_4 (95–97%), tetra-amine platinum(II) chloride hydrate [$Pt(NH_3)_4Cl_2 \cdot xH_2O$, 99.95%], and sodium borohydride ($NaBH_4$, 98%) were purchased from Tedia, Acros, Merck, Aldrich and Lancaster, respectively. Other reagents used were of analytical grade. N_2 (99.9995%) and NO_2 (485 ppm) in N_2 were purchased from a local gas company (San-Fu Chemical Co., Hsin Chu).

2.2. Preparation of Pt/Nafion® electrode

Platinum was deposited on Nafion® 117 membrane by impregnation–reduction (I–R) chemical plating method [18,19]. The commercially available membrane is ion exchanged with a precursor metal salt [$Pt(NH_3)_4Cl_2 \cdot xH_2O$] solution followed by sodium borohydride ($NaBH_4$) treatment as a reductant material.

2.2.1. Pre-treatment procedure of Nafion® membrane

The membrane was immersed in methanol (99.99%) to swell for 2 h. After rinsing with de-ionized water (DIW), the membrane was again treated with 3 wt.% H_2O_2 at 100°C for 40 min to remove organic substances. After intermittent ultrasonic washings, the same membrane was put in 1 M H_2SO_4 at 100°C for 30 min to eliminate the metallic impurities. After final washings with DIW, this pre-treated membrane was used for making a Pt/Nafion® electrode using the impregnation–reduction method.

2.2.2. Impregnation–reduction method for making a Pt/Nafion® electrode

The pre-treated Nafion® membrane was assembled in a glass impregnation–reduction apparatus and kept it in a water bath at 40°C. The membrane was equilibrated with 0.02 M $Pt(NH_3)_4Cl_2 \cdot xH_2O$ aqueous solution for 6 h resulting in Pt ion impregnation. The membrane was washed several times with DIW and kept in 0.1 M NaOH solution adding with 0.05 M $NaBH_4$ for 1 h. After removing the basic solution, the membrane was washed with DIW and finally kept in 0.5 M H_2SO_4 for 30 min to ensure the complete elimination of basic impurities. After final washings with DIW, the Pt/Nafion® electrode was considered for sensing measurements.

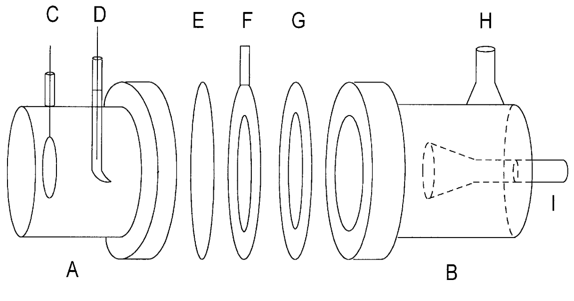
2.3. Configuration of the sensor system

The Pt/Nafion® electrode prepared as described above was used as a working electrode and as a separator to divide the electrochemical cell into a gas (or anodic) chamber and a liquid (or cathodic) chamber. The liquid chamber was charged with H_2SO_4 (0.5 M) aqueous solution and a platinum disk was placed in the aqueous solution to serve as a counter electrode. The reference electrode Ag/AgCl/KCl (sat.) was placed close to the backside of the working electrode. The platinum O–ring was placed in contact with the working electrode as the current collector and another O–ring (made of silicon rubber) was used to prevent the leakage of gas and aqueous solution. A cross-section view of three-electrode system using a Pt/Nafion® electrode is shown in Fig. 1. The electrochemical measurements were performed at room temperature in a three-electrode configuration cell using a potentiostat/galvanostat (EG & G, model 273A).

For all measurements, the geometric area of the Pt/Nafion® electrode used was 3.14 cm^2. The gas flow rate was controlled by a mass-flow meter controller (Sierra 902C). Fig. 2 shows a schematic of the electrochemical oxidation of NO_2 on the Pt/Nafion® electrode.

2.4. Pre-treatment of Pt/Nafion® electrode

The pre-treatment of a Pt/Nafion® sensing electrode has three steps. Firstly, the sensing electrode was put in 485 ppm NO_2 (in N_2 atmosphere) for 3 h by applying 1.05 V to ensure



A: liquid chamber (0.5M H_2SO_4)

B: gas chamber (NO_2 in N_2)

C: counter electrode (Pt, diameter =1 cm)

D: reference electrode [Ag/AgCl/KCl (sat.)]

E: working electrode (Pt/Nafion® electrode)

F: platinum current collector (o. d. =3.0 cm, i. d. =2.2 cm)

G: Silicon O-ring; H: output gas; I: input gas

Fig. 1. A cross-sectional view of three-electrode based Pt/Nafion® gas sensor.

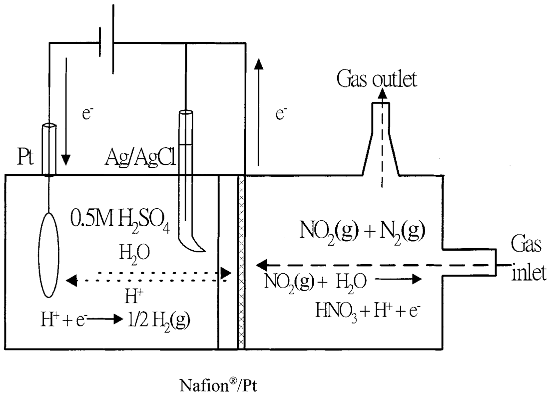


Fig. 2. A schematic representation of the electrochemical oxidation of NO_2 on the Pt/Nafion® electrode.

a steady oxidant current. Secondly, the N_2 was passed for 1 h to remove absorbent NO_2 from the sensing electrode in the potential range from –0.20 to 1.40 V at a rate of 20 mV/s using cyclic voltammetry. Finally, the Pt surface of the sensing electrode was cleaned by passing N_2 for 5 h at 1.05 V.

3. Results and discussion

3.1. Effect of the electrode potential

Fig. 3 shows the steady-state polarization (current density versus potential or *I–E*) curve of the oxidation of NO_2 at Pt/Nafion® electrode. The *I–E* curve for NO_2 concentration (485 ppm) was obtained by initially potentiostating the Pt/Nafion® electrode at 0.90 V for 45 min. The current density was then measured for N_2 and subsequently for NO_2 concentration (485 ppm) at a flow rate of 200 ml/min. The potential of the Pt/Nafion® electrode was then increased to 1.25 V and the steady current at each potential was measured after potentiostating for 45 min (0.90–1.05 V) and for 75 min (1.10–1.25 V). The net oxidation current density of NO_2 as a function of the applied potential is recorded in Fig. 3. It can be seen that NO_2 was oxidized at the Pt/Nafion® electrode when the potential was greater than 0.90 V for 485 ppm NO_2 in N_2. The operating potential range for the NO_2 sensor was found to be 0.95–1.20 V but at a higher potential (1.25 V) the evolution of oxygen gas occurred at the Pt/Nafion® electrode. The working electrode was maintained at a fixed potential with respect to the reference electrode preferably from 0.95 to 1.10 V. The net current density in Fig. 3 increased from 38 to 44 μA/cm^2, a limiting value, when the operating potential was increased from 0.90 to 0.95 V by passing NO_2 (485 ppm) in N_2 at a flow rate of 200 ml/min. One of the possible origins of the background current density in N_2 observed can be explained by a Pt/Pt–O reaction [21]

$$\mathrm{Pt} + \mathrm{H_2O} \Leftrightarrow \mathrm{Pt{-}O} + 2\mathrm{H}^+ + 2\mathrm{e}^- \tag{4}$$

Where Pt–O represents a layer of adsorbed oxygen atoms on the Pt surface. This Pt/Pt–O reaction favoured the operating potential range (0.90–1.10 V) at Pt/Nafion® electrode. Beyond 1.10 V, a layer of oxide, PtO, was formed. Another possibility for the constant background current up to a potential of 1.10 V maybe an unknown leakage current.

3.2. Flow rate effect

For the present NO_2 sensor, the gas flow rate may have a direct effect on the oxidant current density output of the NO_2 sensor. Fig. 4 shows the typical flow-rate effect on the Pt/Nafion® electrode sensing for NO_2 (485 ppm) in N_2 at 1.05 V. The net oxidizing current density reached a diffusion-limit value at a flow rate higher than 200 ml/min, therefore, the flow rate was maintained at 200 ml/min to ensure the diffusion-limit condition. Limiting current density (as shown in Fig. 4) was increased from 22 to 37 μA/cm^2

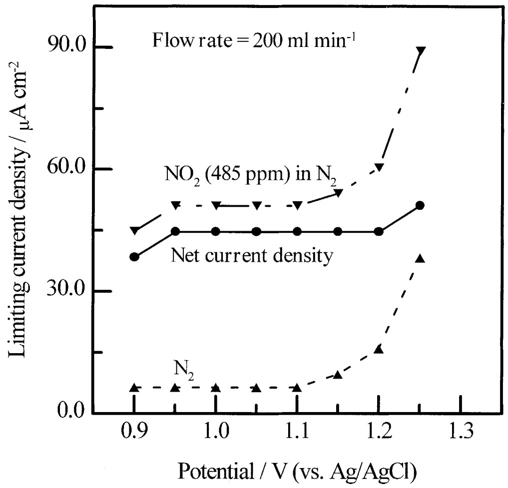


Fig. 3. Limiting current density–potential (*I–E*) curve of the oxidation of NO_2 (485 ppm) at the Pt/Nafion® electrode.

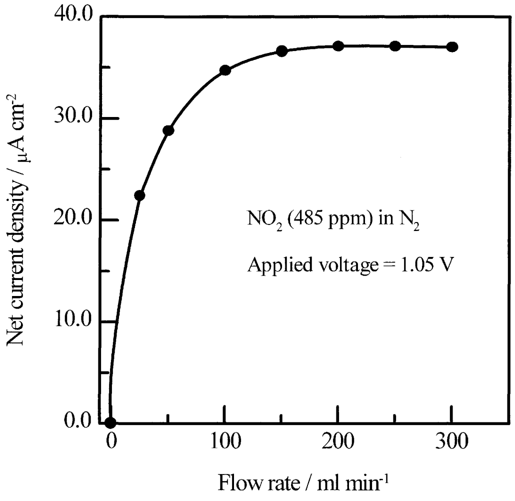


Fig. 4. Plot of net current density vs. flow rate on the Pt/Nafion® electrode sensing for NO_2 (485 ppm) in N_2 at 1.05 V.

at 1.05 V when the flow rate increased from 25 to 200 ml/min. These results were satisfied by Eq. (5), in which the limiting current density can be expressed by [20]

$$I_{\mathrm{lim}} = \frac{nFDC_{\mathrm{NO_2}}}{\delta} \tag{5}$$

where I_{lim}, n, F, D, $C_{\mathrm{NO_2}}$ and δ are the limiting current density, number of transferred electrons, Faraday constant, the diffusivity of NO_2, the concentration of NO_2 in the bulk phase and the diffusion layer thickness, respectively. Therefore, the NO_2 sensor must have a direct relation between the current density and the flow rate.

3.3. Response time and recovery time

The response time (and recovery time) is defined as the time necessary to attain 95% (5%) of the full response time upon a step increase (decrease) in the NO_2 concentration. The response time and recovery time of the Pt/Nafion® electrode for NO_2 (485 ppm) was recorded for three sensing cycles (see Fig. 5). It was observed that the reproducibility of the current density response of Pt/Nafion® sensor was found to be reasonably good. The response time (t_{95}) was achieved in 45 s whereas its recovery time (t_{95}) was 54 s at 1.05 V, when a step change in concentration of NO_2 from 0 to 485 ppm and 485 to 0 ppm was applied simultaneously.

3.4. NO_2 concentration effect

The effect of the NO_2 concentration (0–100 ppm) on the Pt/Nafion® sensing electrode was studied by applying a constant potential (1.05 V) with a gas flow rate of 200 ml/min. Fig. 6 is a typical plot of the current density vs. time for the Pt/Nafion® electrode using different concentrations of NO_2 gas (0–100 ppm). According to Fig. 6, the steady-state current density at 0 ppm was 1.0 μA/cm² but increased to 6.4 μA/cm² at 100 ppm NO_2 concentration, and vice versa.

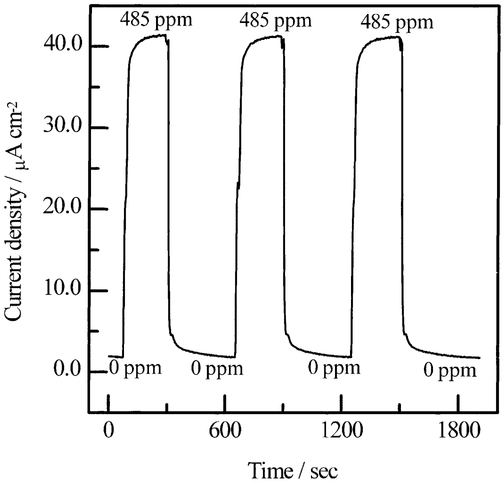


Fig. 5. Plot of current density vs. time for three NO_2 sensing cycles (485 ppm) at the Pt/Nafion® electrode.

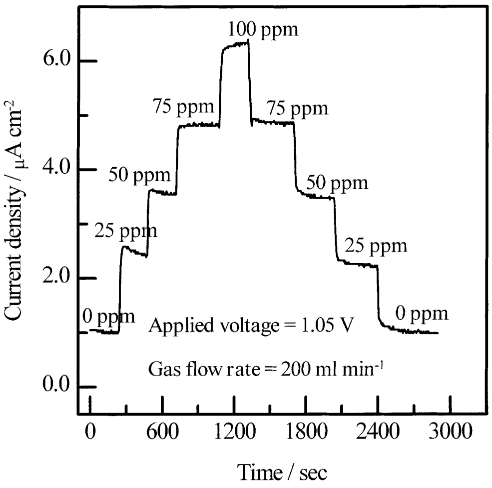


Fig. 6. Plot of current density vs. time for the Pt/Nafion® electrode using different concentrations (0–100 ppm) of NO_2 gas.

Fig. 7 shows the net limiting current density for NO_2 sensing with a Pt/Nafion® electrode. This was calculated in the range of 0–100 ppm NO_2 concentration with the help of Fig. 6. The reproducibility of the experimental data was verified 4 times at each concentration level, as indicated by the error bars in Fig. 7. The sensitivity of Pt/Nafion® electrode for NO_2, measured in the range of 0–100 ppm, is determined from the slope and is 0.16 μA/ppm or 52 nA/ppm/cm². A simple calculation from Fig. 3 or Fig. 5 reveals that the sensor response is nonlinear beyond 100 ppm NO_2.

3.5. Long-term stability

The long-term stability of the Pt/Nafion® based NO_2 gas sensor was tested near 30 days (see Fig. 8) at 100 ppm concentration by applying a potential (1.05 V) and a gas flow rate of 200 ml/min. After 1 day, the net current density rapidly decreased to 4.9 μA/cm² (74% of its initial value,

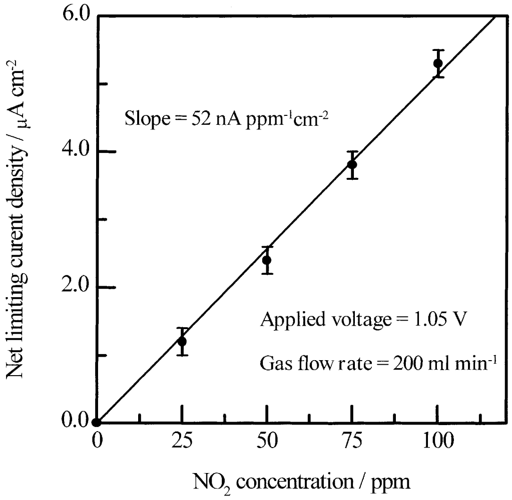


Fig. 7. Net limiting current density vs. NO_2 concentration in the range of 0–100 ppm for sensitivity measurement.

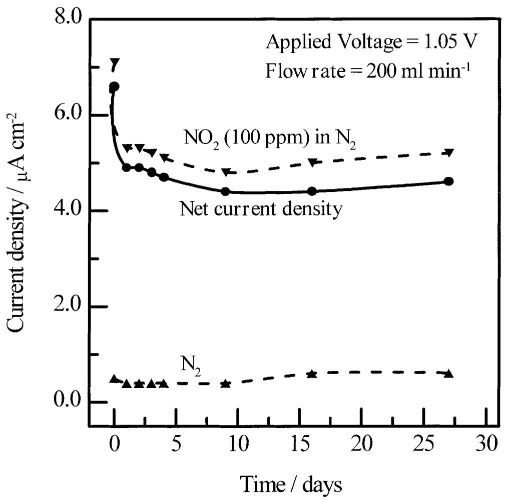


Fig. 8. Plot of limiting current density vs. time (days) for the long-term stability of the Pt/Nafion® based NO_2 sensor.

6.6 μA/cm^2) but after 9 days the current density decreased to 4.4 μA/cm^2 at a slow rate (67% of its initial value) and remained relatively stable for the next 18 days. The decrement (0–33%) in net current density may be due to the oxide formation at the Pt surface [22] which diminished the electrode activity, and consequently lead to an overall decay in the NO_2 sensor output current.

4. Conclusion

A sensor consisting of a Pt/Nafion® electrode at which the NO_2 sensor was oxidized at room temperature by applying a constant potential (1.05 V) was described. The operational potential of the NO_2 sensor showed the best response between 0.95–1.20 V. The response time (t_{95}) and recovery time (t_{95}) of the sensor were 45 and 54 s, respectively when a step change in concentration from 0 to 485 and from 485 to 0 ppm was applied. A linear curve was obtained from 0 to 100 ppm NO_2 concentration and its sensitivity was 0.16 μA/ppm or 52 nA/ppm/cm^2 for 3.14 cm^2 geometrical area of Pt/Nafion® sensing electrode. Thus, an amperometric NO_2 gas sensor based on Pt/Nafion® electrode can be a potential candidate for the sensor industry.

Although, this work reports on successful oxidation of NO_2 on a Pt/Nafion® electrode and raises the potential for the possible application in NO_2 sensing, the sensor response to some other gases such as NO and CO needs to be carried out in order to assess if this sensor is truly sensing NO_2. The cross-sensitivity studies on potential interferants are underway to verify this.

Acknowledgements

The financial support, provided by the National Research Council of the Republic of China under contract numbers NSC 87-2214-E002-017 and NSC 87-EPA-P002-004 is acknowledged. Helpful discussions with Mr. Jin-Cherng Yang and Dr. Pradeep K. Varshney are appreciated.

References

[1] A. Fontijn, A.J. Sabadell, R.J. Ronco, Homogeneous chemiluminescent measurement of nitric oxide with ozone, Anal. Chem. 42 (1970) 575–579.
[2] Y. Maeda, K. Aoki, M. Munemori, Chemiluminescence method for the determination of nitrogen dioxide, Anal. Chem. 52 (1980) 307–311.
[3] R. Chand, Apparatus for measuring nitrogen oxide concentrations, US Patent 3,622,487 (1971).
[4] K.F. Blurton, J.M. Sedlak, Method for the detection and measurement of nitric dioxide and mixtures thereof, US Patent 4,052,268 (1977).
[5] K.F. Blurton, J.M. Sedlak, Device for the detection and NO and NO_2 gases, US Patent 4,001,103 (1977).
[6] J.S. Do, R.Y. Shieh, Electrochemical nitrogen dioxide gas sensors based on solid polymeric electrolyte, Sens. Actuators B 37 (1996) 19–26.
[7] F. Opekar, An amperometric solid-state sensor for nitrogen dioxide based on a solid polymer electrolyte, Electroanalysis 4 (1992) 133–138.
[8] S.C. Chang, J.R. Stetter, Electrochemical NO_2 gas sensor: model and mechanism for the electroreduction NO_2, Electroanalysis 2 (1990) 359–365.
[9] J.R. Stetter, R.B. Cromer, Gas sensing unit, US Patent 4,302,315 (1981).
[10] J.M. Sedlak, K.F. Blurton, The electrochemical reactions of carbon monoxide, nitric oxide, and nitrogen dioxide at gold electrodes, J. Electrochem. Soc. 123 (1976) 1476–1478.
[11] J.M. Sedlak, K.F. Blurton, A new electrochemical analyser for nitric oxide and nitrogen dioxide, Talanta 23 (1976) 811–814.
[12] K.F. Blurton, J.M. Sedlak, Method for the detection and measurement of noxious gases, US Patent 4,042,464 (1977).
[13] J. Langmaier, F. Opekar, Z. Samec, Amperometric solid-state NO_2 sensor based on plasticized PVC matrix containing a hydrophobic electrolyte, Sens. Actuators B 41 (1997) 1–6.
[14] N. Miura, G. Lu, N. Yamazeo, High temperature potentiometric/amperometric NO_x sensors combining stabilized zirconia with mixed-metal oxide electrode, Sens. Actuators B 52 (1998) 169–178.
[15] J.D. Allen, An absolute galvanic detector for nitrogen dioxide, Analyst 99 (1974) 765–770.
[16] Y. Shimizu, K. Maeda, Solid NO_x sensors using pyrochlore-type oxide electrode, Sens. Actuators B 52 (1998) 84–89.
[17] N. Rao, C.M.V. Bleek, J. Schoonman, Potentiometric NO_x sensor with alumina as solid electrolyte and Ag metal as solid reference, Solid State Ion. 52 (1992) 339–346.
[18] P.S. Fedkiw, W.-H. Her, An impregnation–reduction method to prepare electrodes on Nafion® SPE, J. Electrochem. Soc. 136 (1989) 899–900.
[19] P. Millet, F. Andolfatto, R. Durand, Preparation of solid polymer electrolyte composites — investigation of the precipitation process, J. Appl. Electrochem. 25 (1995) 233–239.
[20] S.C. Chang, J.R. Stetter, C.S. Cha, Amperiometric gas sensors, Talanta 40 (1993) 461–477.
[21] J.P. Hoare, The Electrochemisty of Oxygen, Wiley, New York, 1968 34 p.
[22] K.F. Blurton, J.M. Sedlak, The electro-oxidation of carbon monoxide on platinum, J. Electrochem. Soc. 121 (1974) 1315–1317.

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. He has applied surface science/ interfacial engineering and electrochemistry/electrochemical engineering principles for improving the performances of sensor devices, with emphasis on electrochemical, at rest, and thermal stabilities. 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 there.

Wen-Tung Hung received his BS degree in Chemical Engineering from National Taiwan Institute of Technology (currently, renamed as National Taiwan University of Science and Technology), Taipei, Taiwan in 1993. The same year he joined Institute of Oceanography at National Taiwan University as a project assistant. He received MS degree in Chemical Engineering from National Taiwan University in 1996. Currently, he is a PhD candidate at the Department of Chemical Engineering, National Taiwan University. His research interest mainly is in electrochemical sensors. He has published several papers in international environmental journals.