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Investigation of Voltammetric Reduction Profile of N_2O on Platinum Working Electrode

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ABSTRACT: This paper reports the development of N_2O voltammetric sensor that focused on optimization of potential scan rate and concentration of electrolyte, as well as evaluation of the presence some interfering gases. Pt microelectroda, Au metal wire and mini Ag/AgCl serve as the working, counter and reference electrode respectively. Solution of tetrabutyl ammonium perchlorate in dimethylsulfoxide (0.010, 0.025, 0.050, 0.075, 0.100, and 0.150 M) was used as electrolyte solution. The scan rate applied to the working electrode was varied: 20, 40, 60, 80, 100, and 200 mV/sec, in the potential range of 0.0 to -2.8 volts. O_2 and CO_2 were chosen as the interfering gases as their presence in the ambient air are very dominant. The optimum sensor response was achieved at a scan rate 100mV/sec and concentration of 0.100 M TBAP and able to work well on N_2O gas concentration range from 4% to 20%. O_2 was found as main interference, however CO_2 was not providing a significant interference response to the sensor.

Keywords: nitrous oxide, voltammetry, electrochemical sensor, platinum microelectrode

INTRODUCTION

The most abundant oxide of nitrogen in the atmosphere is nitrous oxide, N_2O, and well known as laughing gas. Mostly, nitrous oxide in the atmosphere is formed by microbes in the soil by a process known as denitrification, in which valuable plant nutrients are lost as certain soil microorganism use nitrate instead of nitrogen in order to respire, forming nitrous oxide and nitrogen. A few amounts of nitrous oxide are also produced by the process of nitrification as a result of incomplete conversion of ammonium to nitrite.[1] In the industrial countries, a major source of nitrous oxide was the production of adipic acid,[2] others sources of nitrous oxide emission are from fuel combustion,[3] from motor vehicles, and from agriculture activities.[4]

Nitrous oxide has been widely employed as both an anaesthetic and an analgesic agent for hundred years. It has been adopted as an anaesthetic carrier gas on anaesthetic machines used in clinical practice. It is used as an analgesic agent in obstetric medicine, usually administered during labour.[5] In food industry, it is utilised as a propellant for pressurised container containing food-stuff.[6]

Currently, nitrous oxide is considered as a potential destroyer of the ozone layer, so it has gained new scientific and political importance as a greenhouse gas.[7] Increasing human awareness about the contribution of nitrous oxide on global warming has made people attention to the concentration profile and the emission profile of nitrous oxide is also higher. The profile of concentration and emission of nitrous oxide over period of certain time on specific geographical location is a set of useful information for predicting future concentration or emission and then for mitigating the pollution effect of the nitrous oxide to the environment.

According to various type of sources and application of nitrous oxide, as mentioned above, the measuring devices are necessary for detecting nitrous oxide in wide range concentration namely from ppb to per cent levels. Current measurement techniques for nitrous oxide are infrared spectroscopy[8,9] or gas chromatography.[10,11] This paper is explaining current work on development of electrochemical voltammetric sensor targeted for direct measurement of concentration as well as emission of nitrous oxide gas.

METHODS AND EXPERIMENTAL DETAILS

Voltammetric profile of the nitrous oxide reduction was carried out in an electrochemical cell comprises of three electrodes: a working electrode (WE), a reference electrode (RE) and counter electrode (CE). The cell was constructed from a glass-sealed platinum microelectrode (CH Instruments) with diameter of 10um, a gold wire with diameter of 0.5 mm (Aldrich) a mini Ag/AgCl (CH Instruments) as WE, CE and RE respectively. The three electrodes were then housed in a set of three part of PTFE tubes: top cover, main body and bottom stopper (Figure 1). One end of the cell was covered with a 25 um PTFE membrane (Membrane Solution). An O ring was used for tightening the membrane onto the PTFE house and secured by the stopper at the bottom part of the cell. The filling solution of the electrode was a non-aqueous electrolyte, tetrabutylammonium perchlorate, TBAP (Aldrich) in dimethylsulphoxide, DMSO (Fluka) at various concentrations (0.010, 0.025, 0.050, 0.075, 0.100, and 0.150 M).

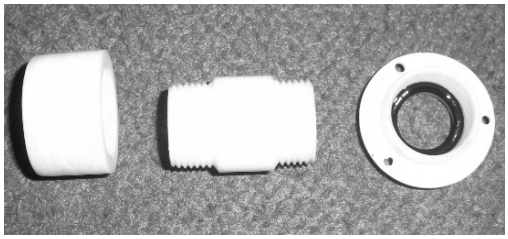

Figure 1. PTFE cell housing

Voltammetric investigation of the cell was carried out by similar method in previous work.[12] A computer controlled potentiostat Amel 433A was used as main instrument for electrochemical characterization. Potential polarization in a form of cyclic voltammetry mode was applied in the range of potential 0.00 to -2.80 volts against Ag/AgCl reference electrode at various potential scan rate (20, 40, 60, 80, 100, and 200 mV/sec). A set of mass flow controllers (Horiba) was used for controlling the gas mixing. All gases (nitrous oxide, nitrogen, oxygen and carbon dioxide) used in this work was UHP grade (PT. Aneka Gas Industri). The gases were then delivered at certain flow-rate into the glass-sealed containers in which the electrochemical cell was placed (Figure 2).

RESULTS AND DISCUSSION

The concentration of TBAP in DMSO solvent was varied in the range of 0.010 – 0.15 M. There was evidence that the concentration of the electrolyte affects the electrochemical reaction in the system as indicated by the obtained voltammograms of each TBAP concentration using (Figure 3).

Figure 2. Three-electrode system of the electrochemical cell placed in the sealed glass container

Generally, the lower concentration the lower the current produced as a result of a change in conductivity of the electrolyte. The reduction current of the nitrous oxide was quite clearly shown even if the current response did not plateau form. In other words, conductivity plays an important role in the reaction. However, it does not mean that the higher conductivity the better sensor response, as can be seen in the following evidence. The best concentration of TBAP was 0.10M for the Pt electrode as shown in the corresponding voltammogram.

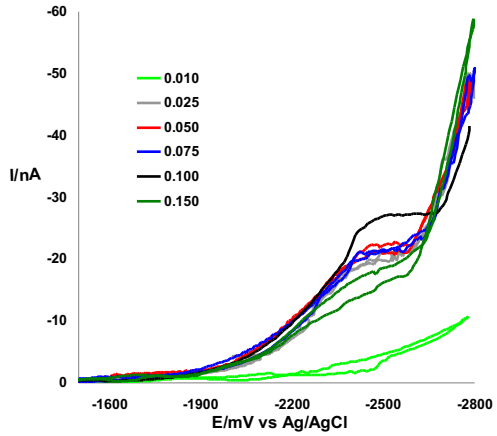

Figure 3. Series voltammograms of N_2O reduction on Pt electrode at various TBAP concentrations.

Variation of potential scan-rate to the electrode has indicated that scan-rate of 100 mV/s is the best value for the corresponding working electrode in reducing the nitrous oxide. Superiority of this rate was not just the magnitude of the resulted current; it was also corresponding to the quality of the voltammogram. Most of other scan-rate has resulted fluctuated current responses. As the resulted current is consequence of the nitrous oxide availability on the diffusion layer closest to the working electrode, hence the best scan-rate (100 mV/s) probably the matching value of polarization rate correspond to the surface area of the

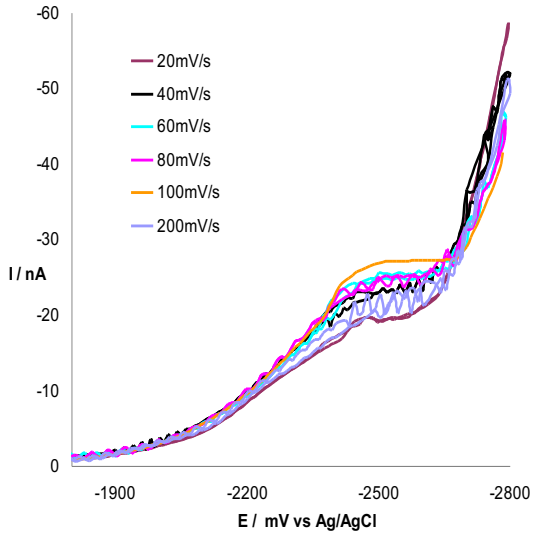

Figure 4. Series voltammograms of N_2O reduction on Pt electrode at various potential scan-rate

working electrode and diffusion rate of the nitrous oxide at corresponding solvent and electrolyte concentration. It should be note that this optimum value would not always suitable for all platinum electrodes when their surface area very large (e.g. Pt macroelectrode).

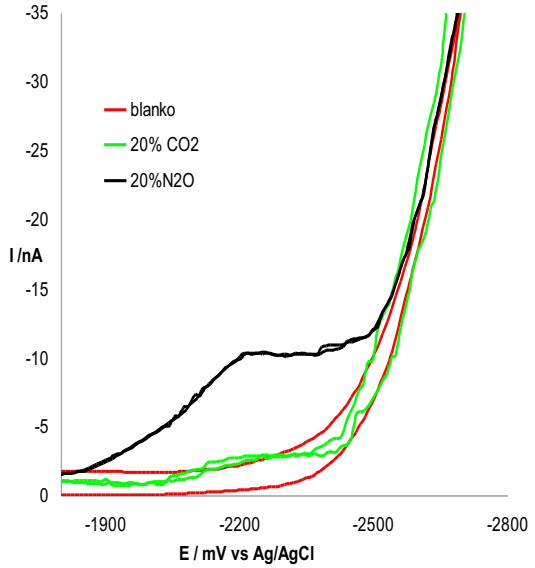

Figure 5. Series voltammograms of N_2O and CO_2 reduction on Pt electrode.

Figure 5 and 6 has shown interference effect of carbon dioxide and oxygen on reduction potential range corresponding to nitrous oxide. According to these figures, the interference effect of oxygen can be said slightly higher that carbon dioxide. Reduction peak that affected by presence of oxygen is clearly indicated. A more comprehensive investigation to this interference gases is suggested to be carried out to assure that Pt electrode can be implemented as nitrous oxide sensor and relatively free from interferences.

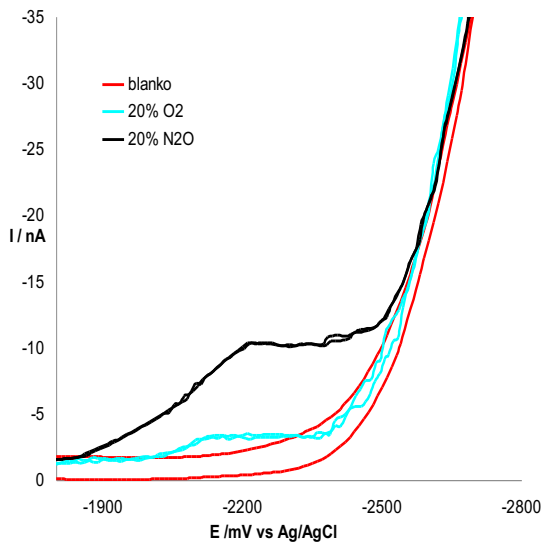

Figure 6. Series voltammograms of N_2O and O_2 reduction on Pt electrode

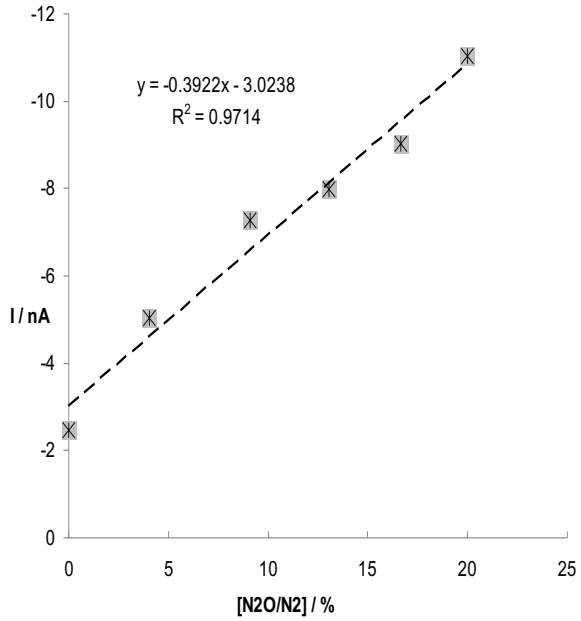

Figure 7. Calibration curve of current response of the Pt working electrode at various percentage of nitrous oxide

Characterization result of the Pt electrode in responding to various concentration of the nitrous oxide is presented in Figure 7. At the optimum condition (scan rate 100mV/sec, [TBAP] 0.100 M TBAP) the platinum electrode was capable to work fairly well on N_2O gas concentration range from 4% to 20%. Linearity response of the Pt electrode, as shown in this figure, is not excellent. It is probably caused by resolution of the potentiostat used in this work. Usually this type of potentiostat is dedicated for use with macroelectrode resulting a relatively higher current that in the suitable range of current resolution of the potentiostat.

CONCLUSION

Platinum microelectrode has shown its capability to be used as a core component in development of nitrous oxide sensor. Further investigation is needed to improve its performance, e.g. sensitivity and linearity response. A low current-sensitive potentiostat is required when using a microelectrode.

Acknowledgments

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