

Gas Sensor with Pt/Nafion Electrodes

Masao Ishikawa and Seimei Shiratori

Department of Applied Physics and Physico-Informatics Faculty of Science and Technology Keio University,
3-14-1 Hiyoshi Kouhoku-ku Yokohama Kanagawa 223-8522 Japan
Fax: 045-561-1602, e-mail: ishimasa@appi.keio.ac.jp

Abstract

Electrochemical gas sensor for monitoring gas emitted by everyday life, for example methylmercaptan, trimethylamine, acetic acid, acetaldehyde and ethylene gas, is described. Sensing electrodes of this sensor were fabricated by chemical deposition of platinum on cation exchange Nafion membrane that was well known as a solid polymer electrolyte (SPE) of a fuel cell (PEFC). The sensing electrodes (Pt/Nafion electrodes) were produced with various conditions and evaluated SEM, AFM and XPS. Then the optimum electrode was determined. We evaluated influence of real surface area of Pt/Nafion electrodes, flow rate of gas, sensibility of sensor response and selectivity. These results shown that methylmercaptan had high selectivity in potential range from 0.6 to 1.2V vs.Ag/AgCl and this reaction was dominated by the mass transport because it was thought that the electrochemical reaction on the Pt/Nafion electrode is the fast reaction kinetics. Therefore, this sensor is expectable for sulfur combination, for example bad breath sensor.

Key words: gas sensor, platinum, Nafion, methylmercaptan

1.INTRODUCTION

The sensors that analysis gas had been reacted on electrodes of an electrochemical sensor were has remarkable development. These sensors are usually based on a gas-permeable membrane such as porous poly tetrafluorethylene (PTFE) bearing a precious metal electrode on the side that is contact with an internal electrolyte solution. The analysis gas diffuses through the non-wetted pores in a non-selective manner. Sensors based on such gas-diffusion electrodes have been commercially available for some time for monitoring of a number of toxic species.

A basically different arrangement is based on metallized ion-exchange membranes (solid polymer electrolyte: Nafion etc. Figure1 shows structural of Nafion membrane.) with electrodes on the front side. This means that the analysis gas does not have to diffuse through the membrane in this case and the mass transport rate to the electrodes can be expected to be high.

In recent years, as a living standard improves, life smells such as refrigerator, garbage disposal and bad breath have attracted attention. Most of electrochemical gas sensor used permeability film had been commercialized, however the detection limit and selectivity was not enough. Moreover, most of electrochemical gas sensor used solid polymer electrolyte may be performed at high temperature (500 degree), since conductivity of a solid polymer electrolyte is very low at low temperature. However, since the analysis gas in this research was life smells, we aims at measurement in normal temperature. Five kinds of gas were chosen for this study (methylmercaptan: the decomposition smell of meat, trimethylamine (TMA): the decomposition smell of a fish, acetic acid: vinegar, acetaldehyd: smoke of tobacco and ethylene: vegetable growth hormone).

Before we changed the solution concentration at the time of producing Pt/Nafion produced the optimum

electrode. Furthermore in the domain beyond voltage 0.6V vs.Ag/AgCl, we observed about ethylene gas and evaluated influence of real surface area of sensing electrodes, flow rate of gas, sensitivity of sensor response and selectivity. And we have known that response current of ethylene gas was not so good. However, by this experiment, we were able to obtained the response current of methylmercaptan. Therefore this sensor is expectable for sulfur combination, for example bad breath sensor.

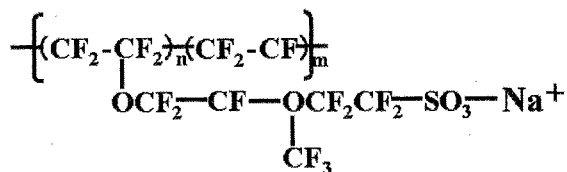


Fig.1 Structural of Nafion membrane

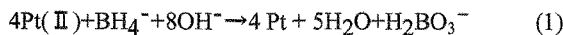
2.EXPERIMENTAL SECTION

Solid polymer electrolyte employed was a Nafion membrane. The deposition of porous platinum surface onto Nafion was carried out via the chemical reduction of a platinum salt. Tetraamineplatinum(II) chloride and sodium borohydride were estimated as the sources of platinum and reducing agent, respectively.

Before depositing platinum on Nafion membrane, the Nafion membrane was cut in one side size of 2.5cm and immersed for 30 minutes into nitric acid solution. Then Nafion soaked in 70°C pure water for 5 hours. These pretreatments were process for removing dirt and impurities of Nafion membrane surface. The Nafion membrane was placed in the cell for impregnation filled with tetraamineplatinum (II) chloride solution for 40 minutes. After impregnation step, the platinum solution was removed from the cell and replaced the reducing

solution. In this reduction step, the solution was stirred with 200 rpm for 120 minutes. After the reduction step was completed, the produced Pt/Nafion electrodes were soaked in sulfuric acid solution of 1M and saved normal temperature in the pure water.

Changing the electrochemical surface area of Pt/Nafion electrodes, it obtained mainly by changing platinum salt concentration, reducing solution concentration and churning speed of solution. In this experiment, we obtained different surface area of Pt/Nafion electrodes via changing reducing solution concentration. The equation of platinum deposit process is shown in the following (1).



The determination of the electrochemical surface area of Pt/Nafion electrodes was estimated from the charge of the hydrogen adsorption region of the cyclic voltammogram after subtracting the double-layer charge.

The design of the electrochemical sensor is shown in Figure 2. The cell enables contact of Pt/Nafion electrode with a flowing gas stream and the back with the electrolyte. geometric working electrode area exposed to the gas stream was 0.79 cm^2 ($\phi=10\text{mm}$). The reference electrode (RE) was Ag/AgCl electrode. Platinum plate and sulfuric acid solution of 1M were used as counter electrode (CE) and internal electrolyte solution respectively. The platinum mesh was used as current collector. A mixture of analysis gas/nitrogen (<10 ppm) was passed to sensing electrode chamber with flow rate from 50 to 300 ml/min.

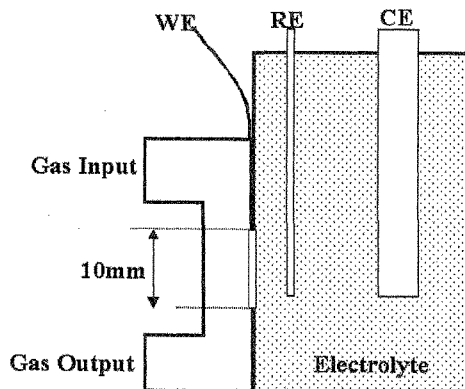


Fig.2 Schematic view of the sensing cell, WE: Pt/Nafion electrode, RE: Ag/AgCl electrode, CE: platinum plate, Electrolyte: sulfuric acid solution of 1M

3.RESULT AND DISCUSSION

Surface of Pt/Nafion electrode

SEM observation photograph of the Pt/Nafion electrode surface is shown in Figure 3-1 and Figure 3-2. The former electrode (Figure 3-1) was produced with low concentration of reducing agent and was not uniform with platinum. It is thought that the black portion on the right-hand side of a photograph indicates the surface of Nafion membrane. Moreover, the white portion on the left-hand side of a photograph indicates grew platinum particle on Nafion membrane. On the other hand, the latter electrode (Figure 3-2) was produced with high

concentration of reducing agent. This photograph shows that precise structure with which the platinum particle grew and became entangled is observed.

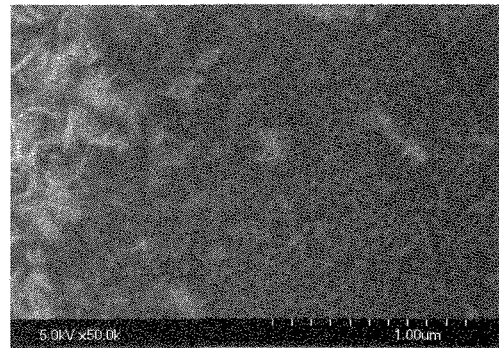


Fig.3-1 Scanning electron micrograph (SEM) of surface of Pt/Nafion electrode with low concentration of reducing agent

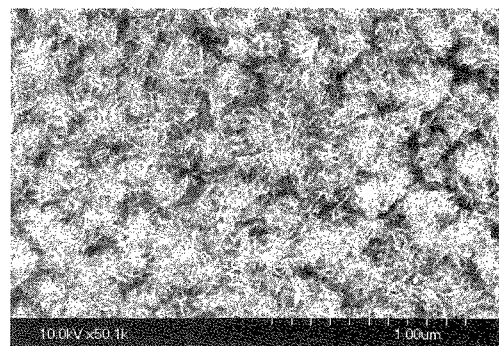
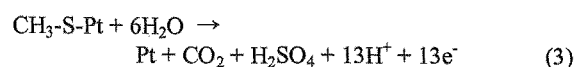
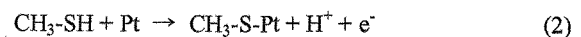


Fig.3-2 high concentration of reducing agent

Influence of potential and selectivity

Figure 4 shows the steady state polarization (current density versus potential or I-E) curve of the oxidation of methylmercaptan, TMA, acetic acid, ethylene and acetaldehyde at Pt/Nafion electrodes. Vertical axis indicates the response current for each gas after subtracting the current for nitrogen. It shows that the response current of methylmercaptan was large as compared with other gases at potential from 0.6 to 1.2V vs.Ag/AgCl because it is thought that the electrochemical reaction happened after the mercapto groups adsorbed peculiarly on the platinum electrode.

This phenomenon that it is easy to adsorb the mercapto groups and platinum is known well. Therefore, as soon as methylmercaptan gas reached the Pt/Nafion electrode, the mercapto groups adsorb the platinum (1). At this time, it is thought that platinum works as a catalyst. After that, the electrochemical reaction happened on Pt/Nafion electrode (3). However, these (2) and (3) are temporary or fictitious process. It is difficult to investigate that if this process is right. In future study, we will investigate change of response current when the concentration sulfuric acid solution is changed.



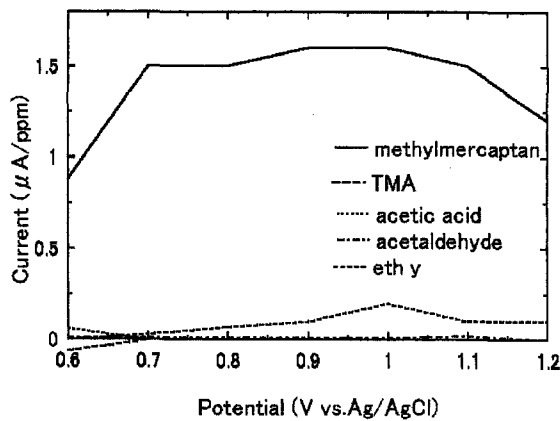


Fig.4 Plots of response currents for methylmercaptan, TMA, acetic acid, acetaldehyde and ethylene in N_2 vs. applied potential at Pt/Nafion electrodes. Real surface areas are 300 cm^2 for Pt/Nafion electrodes; potential from +0.6 to +1.2V vs.AgAgCl at 0.1V intervals; gas flow rate = 50ml/min.

Influence of gas flow rate

Plots of the response current vs flow rate (from 50 to 300 ml/min) for the Pt/Nafion electrode over methylmercaptan gas (0.5, 1.0, 1.5 or 2.0 ppm) is shown in the Figure5. The experimental condition were performed gas flow rate change for 50-300ml/min, 0.5M sulfuric acid as electrolysis liquid, potential of 1.0V vs.Ag/AgCl. When changing flow rate of nitrogen gas, the base line of current didn't hardly changed. Figure5 shows that the current response is also increasing when gas flow rate is increased. Moreover, the current response is increasing when concentration of methylmercaptan gas is increased. However, if gas flux is raised too much, it will be thought that it has immense influence on the increase in noise of a current response and the humidity change on the electrode surface. Therefore, it is necessary to adjust the gas with different relative humidity (RH), and to investigate influence of humidity in future research. As a result, the sensor sensitivity of 200ml of flux was about $7.0\ \mu\text{ A/ppm}$, and it showed one about 6.5 times the sensitivity of this in comparison with flow rate of 50ml/min. It indicates that the detection limited gas concentration was about 100ppb for methylmercaptan.

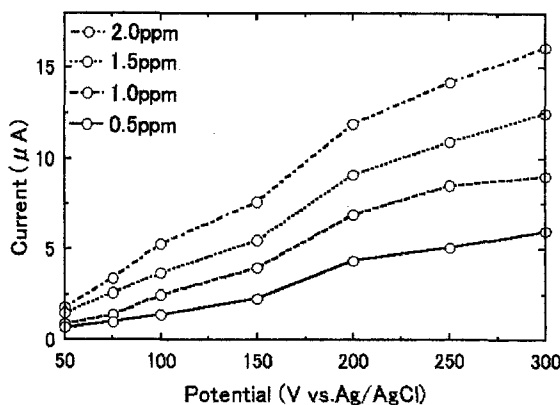


Fig.5 Plots of response current vs methylmercaptan flow rate from 50 to 300 ml/min for methylthiol(0.5, 1.0, 1.5, 2.0 ppm) in N_2 ; +1.0V vs.AgAgCl.

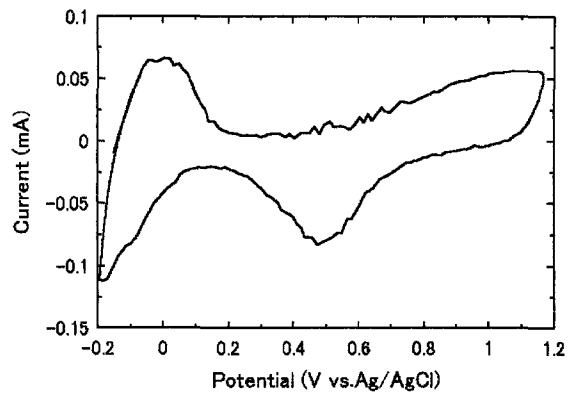


Fig.6 Voltammogram at Pt/Nafion electrode ($A_{\text{real}}=50\text{ cm}^2$) in contact with 1M sulfuric acid, scan rate=32mV/s.

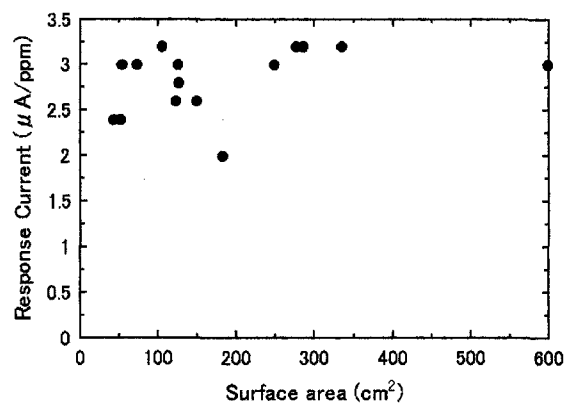


Fig.7 Plots of surface area of Pt/Nafion electrodes vs response current of methylmercaptan, gas flow rate 150ml/min.

Influence of surface area of electrodes

The current response of methylmercaptan on Pt/Nafion electrodes with different surface area is shown in Figure7. The surface area of Pt/Nafion electrodes were calculated from the charges associated with the adsorption of hydrogen from 0.2 to -0.15 V vs.Ag/AgCl in the cathodic sweep of the cyclic voltammogram based on a reported charge density of $210\ \mu\text{ C/cm}^2$ in 1M sulfuric acid, whereas the geometric surface areas were calculated to be $0.79\ \text{ cm}^2$. Figure6 shows a typical cyclic voltammogram of Pt/Nafion electrode. The surface state and the electrochemical reactions involved can be divided according to the applied potential. Anodic sweep direction: ionization of adsorbed hydrogen (-0.2 to 0.0 V vs.Ag/AgCl), electrodeposition of surface oxide (>0.4 V), and water oxidation (>1.2 V). Cathodic sweep direction: reduction of surface oxide (0.8 to 0.4 V) and redeposition of atomic hydrogen (<0.0 V). Double layer charging current is observed (0.05 to 0.3).

Changing the electrochemical surface area of Pt/Nafion electrodes, it obtained mainly by changing platinum salt concentration, reducing solution concentration and churning speed of solution. In this experiment, we obtained different surface area of Pt/Nafion electrodes via changing reducing solution concentration. As shown in Figure7 for methylmercaptan, the dependence on the effective surface area from 50 to $600\ \text{ cm}^2$ is not obtained. The response current was about $3.0\ \mu\text{ A/ppm}$. This

indicates that the reaction of methylmercaptan is dominated by the mass transport from 0 to 200 ml/min because it is thought that the electrochemical reaction on the Pt/Nafion electrode is the fast reaction kinetics.

Response time and stability

The current response when introducing methylmercaptan (1.0 ppm and 10.0 ppm) with flow rate of 150ml/min is shown in Figure 8. When gas concentration was 1.0 ppm, the saturation state current is mostly reached in about 1 minute and desorb was also performed nearly completely in about 1 minute. Besides, in 10.0 ppm, the response reached the saturation state current completely required for about 2 minutes. It is thought that the condition of high concentration spends much time that diffuse to reaction sites of Pt/Nafion electrode. Figure 8 shows that 90% of all current responses is attained in about ten seconds with each gas concentration. It was observed that the reproducibility of the current density response of Pt/Nafion electrode was found to be reasonably good and noises cannot be found. However, it is thought that the spikes of sensor response are noise by gas change between nitrogen and methylmercaptan.

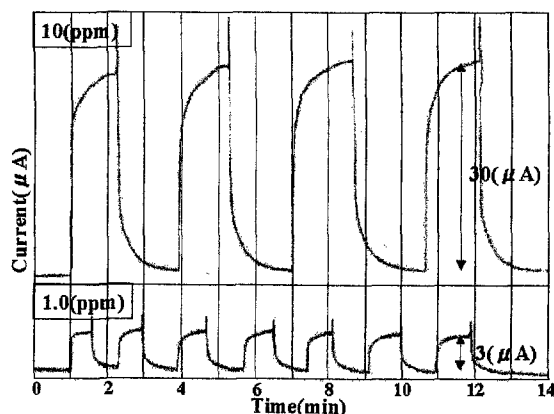


Fig.8 Current vs time profile at Pt/Nafion electrodes for methylmercaptan 1.0ppm and 100ppm in N₂; gas flow rate 150ml/min

4. Conclusion

In this study, the sensor response was performed about methylmercaptan, trimethylamine, acetic acid, acetaldehyde and ethylene. We found that methylmercaptan had high selectivity in potential range from 0.6 to 1.2V vs. Ag/AgCl and this reaction was dominated by the mass transport in flow range 200 ml/min or less. The sensor response time was fast in low gas concentration and detection limited gas concentration with gas flow rate 200 ml/min was 100ppb for methylmercaptan. This sensor is expectable for sulfur combination, for example bad breath sensor.

5. References

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