Electrochemical Detection for Gaseous Vinyl Chloride with a Sputtered Au/Porous Alumina Substrate/Pt Electrode Assembly

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Received: October 8, 2001
Final version: January 16, 2002

Abstract
A detector with a porous alumina substrate has been developed to monitor vinyl chloride gas in the concentration range of 0.5–4% at room temperature successfully. Several operating variables, including type of supporting electrolyte, applied potential, concentration of supporting electrolyte, and porosity of alumina substrate were investigated to find the highest sensitivity for vinyl chloride sensing. Compared with tetrabutylammonium tetrafluoroborate, higher sensitivities were obtained when tetrabutylammonium perchlorate was used as the supporting electrolyte. The highest sensitivity of $70.9 \mu \text{A} \cdot \%^{-1}$ was obtained at $-2.1 \text{ V} \text{(vs. Ag/AgCl)}$ in 50% toluene/50% DMF electrolyte containing 10 mM Bu$_4$NClO$_4$ supporting electrolyte. The sensing current and the sensitivity for vinyl chloride increased significantly with the porosity of the porous alumina substrate.

Keywords: Electrochemical detector, Vinyl chloride monomer (VCM), Porous alumina substrate, Supporting electrolyte, Porosity

1. Introduction
Organic medium has been used in electroanalysis widely. Compared with aqueous medium, organic medium is useful in the determination of organic compounds due to higher solubility and wider applicable potential range. Aprotic solvents, such as dimethylformamide (DMF) and acetonitrile, were generally applied for the solvents, in the presence of appropriate supporting electrolyte, to investigate the reduction or oxidation of electroactive species due to difficulty of solvent decomposition and sufficient stability of electrochemical intermediates [1, 2].

Effects of the medium composition on the reaction current of neutral and charged species in DMF/toluene mixtures have been investigated by Montenegro and co-workers [3]. They demonstrated that changes in the solvent composition and supporting electrolyte concentration yielded different limiting currents for the same concentration of electroactive species because of change in the diffusion coefficient of the electroactive species, accompanied by the change in the medium viscosity. Furthermore, the gaseous electroactive species, hydrogen and oxygen, were dissolved into the organic medium and analyzed [4, 5]. Hahn and co-workers [6, 7] used a gold microdisk electrode to investigate the detection of O$_2$ and CO$_2$ in gaseous phase by using solvent of dimethyl sulfoxide (DMSO), containing supporting electrolyte of 0.1 M Bu$_4$NClO$_4$. The organic medium indeed provided a suitable sensing condition for the reduction of O$_2$ and CO$_2$ with a low background current. Few publications, nevertheless, were found on the effect of electrolyte composition on the sensing performance when the organic medium was applied in gas sensors. The effect of medium composition on the responding current in gas phase might be different from those in liquid phase [3] since diffusion of electroactive species might not be the determining step.

According to the Material Safety Data Sheet [8], vinyl chloride was extremely flammable and has been confirmed to be carcinogenic to humans. It may have effects on the liver, blood vessels, and connective tissue. Approximately 4 percent loss estimate of vinyl chloride monomer (VCM) has been reported [9], based primarily on material balance studies. Losses to the outdoor atmosphere from industrial sources may occur at a large number of valves, flanges, and other components in the manufacturing process. The loss of vinyl chloride gas from manufacturing process could be monitored with detectors at the locations where leakage occurs.

The electrochemical reduction of vinyl halide involved uptake of one electron followed by loss of a halide ion to yield a vinyl radical, which was then protonated and reduced [10]. The rate constant of reduction of vinyl chloride was usually smaller than alkyl halides, e.g., dichloroethane and trichloroethane [11, 12]. In other words, larger kinetic overpotential arose when the electrochemical reduction of vinyl chloride was carried out. Consequently, the amperometric sensing process for vinyl chloride might be controlled by kinetics on the electrode, instead of diffusion of the reactant from the bulk to the electrode surface. The possibility will be increased if the concentration of vinyl chloride in gas is not ultimately low.

Metal oxides have been used as the sensing material in semiconductor sensors [13] and the solid electrolyte in electrochemical sensors [14] at high temperature for many hydrocarbons, such as benzene, chloroform, octane, and methane. Stetter and co-workers [15, 16] used mixture of...
lanthanum salts as sensing material to detect the chlorinated hydrocarbons. Ling and co-workers [17] detected vinyl chloride gas with chemiluminescent method and compared the performance with gas chromatography.

In our previous work [18], an amperometric analyzer was developed to monitor vinyl chloride gas. The configuration was successful in detecting vinyl chloride at appropriate sensing potentials at room temperature in the concentration range of 13 – 44.5%. In the present study, a further focus was on the effects of operating variables on the detection of vinyl chloride gas in lower concentration range, 0.5 – 4%. The variables under investigation included type of supporting electrolyte, applied potential, concentration of supporting electrolyte, and porosity of alumina substrate.

2. Experimental

2.1. Electrode Assembly

The electrochemical sensing cell used in the present study is shown in Figure 1 and has also been described previously [18]. The sensing cell used a porous alumina plate to separate two chambers, filled with electrolyte and test gas. On the sides of the porous alumina plate, gold and platinum films, with the same geometric area of 3.14 cm², were fabricated by sputtering at 5 mA for 10 min and 20 mA for 3 min as the sensing and counter electrodes, respectively. A silver/silver ion electrode (Ag/Ag⁺) with a 0.1 M TBAP/0.01 M AgNO₃/acetonitrile filling solution was installed in the electrolyte chamber as the reference electrode. Detailed information of the characteristics and preparation procedures were described in literature [19]. It’s potential was +0.35 V (vs. saturated calomel electrode, SCE) in DMF containing 10 mM TBAP. All potentials reported in the present study were referred to the potential of the reference electrode. The sensing electrode faced to the test gas and the counter electrode, on the other side of the porous alumina substrate, faced to the electrolyte. In this assembly, the electrolyte permeated through the porous alumina substrate from the electrolyte chamber to the sensing electrode and formed three-phase reacting sites on the surface of sensing electrode. The three-phase reacting sites were the junction of the test gas (gas phase), the electrolyte (liquid phase), and the gold electrode (solid phase), which was available to exert the cathodic reaction of vinyl chloride. To prepare the test gas with a desired concentration, 99.9% vinyl chloride gas was first blended with high purity nitrogen in a mixing bottle, and then passed into the sensing chamber at the constant flow rate of 142 mL min⁻¹. Before vented into the air, the outlet gas from the sensing chamber passed through an absorption setup, composed of solvent and activated carbon columns. All the pipelines from gas cylinders to the vent were connected via ¼ in. Swagelok fitting, adapter, and Tefon tubing and was installed in a hood. The pipelines were checked by using a leak detective liquid (1LD-EF/230, HOKE) before experimenting to avoid any leakage of vinyl chloride gas.

2.2. Measurements of Sensing Current and Porosity of Alumina Plate

Chronoamperometry was applied to determine the current response with and without vinyl chloride. The sensing current was calculated from the difference between the background current in pure N₂ atmosphere and the measured current in VCM/N₂.

The pore volumes of three types of porous alumina plates were determined by nitrogen adsorption at 77 K with an automated adsorption apparatus (ASAP 2010, Micromeritics). Before each analysis, the sample was degassed at
473 K in vacuum at about 10\(^{-3}\) Torr. The total volume were determined at \(p/p_0 = 0.99\). The porosity was reported in terms of the ratio of pore volume to bulk volume.

The characteristics of porous alumina substrates are listed in Table 1. A-1, A-2, and A-3 denotes the three types of substrates. The thickness of sensing electrode film on any type of substrate was estimated around 60 nm, based on the sputtering conditions.

### 2.3. Chemicals and Instrumentation

A potentiostat (273A, EG&G) was applied in the chronoamperometric experiments. A gold ion sputter (JFC-1100, JEOL) and a platinum ion sputter (E-100, HITACHI) were used to fabricate the sensing and counter electrodes, respectively. Mass flow controllers (FC-2901V, Millipore) were used to prepare the desired concentrations of VCM in \(N_2\) by blending VCM (99.9%, Formosa Plastics Co.) and high purity nitrogen with appropriate ratios of flow rates.

The solvent mixture, 50% toluene (HPLC, Tedia)/50% dimethylformamide (HPLC, Tedia) was used without further purification. The supporting electrolytes, tetrabutylammonium perchlorate (Bu\(_4\)NClO\(_4\)) and tetrabutylammonium tetrafluoborate (Bu\(_4\)NBF\(_4\)) were purchased from TCI (Japan). The porous alumina plates were provided by Leatec Fine Ceramics Co. (Taiwan).

### 3. Results and Discussion

In our previous work [18], in the 50% toluene/50% DMF solvent mixture containing 10 mM Bu\(_4\)NClO\(_4\), high sensitivity in detecting vinyl chloride with a moderate background current was observed. The type of porous alumina substrate for the electrode assembly was A-1. At applied potential –2.4 V (vs. Ag/Ag\(^+\)), the sensitivity, response time, and recovery time in 13–44.5% concentration range were 1.90 \(\mu\)A %\(^{-1}\), less than 80 seconds, and within 8 min, respectively.

#### 3.1. Response Curve

In the 50% toluene/50% DMF electrolyte containing 10 mM Bu\(_4\)NClO\(_4\) and at applied potential –2.1 V (vs. Ag/Ag\(^+\)), the current response of Au/A-3 porous alumina plate/Pt assembly under step changes of various concentrations is shown in Figure 2. The assembly was exposed to vinyl chloride gas after the background current reached a constant value. When inlet gas changed from nitrogen to VCM/N\(_2\), the response current increased rapidly to reach a maximum and then decreased to a constant value. The response time for each sensing was decided when the response current did not change for 50 seconds. The response time were between 130 and 150 seconds in the concentration range of 0.5–3% except for the first sensing. A linear relationship between the sensing current and the concentration of vinyl chloride is shown in Figure 4a. Under this condition, the slope, namely the sensitivity, was 70.9 \(\mu\)A %\(^{-1}\). It was around 37 times as large as that in the concentration range of 13–44.5% in our previous work [18]. The significant increase in sensitivity was contributed to both the lower concentration range and larger porosity of porous alumina substrate.

#### 3.2. Polarization Curves

In the 50% toluene/50% DMF electrolyte containing 10 mM Bu\(_4\)NClO\(_4\) with an Au/A-3 porous alumina plate/Pt assembly are shown in Figure 3. The sensing current increased from 0 to 80 \(\mu\)A when the applied potential changed from –1.6 to –2.1 V (vs. Ag/Ag\(^+\)). The electrolyte proceeded cathodic reaction considerably at potentials more negative than –2.2 V (vs. Ag/Ag\(^+\)) with much larger background current. At applied potential –2.2 V (vs. Ag/Ag\(^+\)), the ratio of sensing current to background current was too small for vinyl chloride sensing.

#### 3.3. Effect of Supporting Electrolyte

Two types of supporting electrolyte, tetrabutylammonium perchlorate (Bu\(_4\)NClO\(_4\)) and tetrabutylammonium tetrafluoborate (Bu\(_4\)NBF\(_4\)), were applied to study the effect of

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Table 1. The characteristics of various types of porous alumina substrates.

<table>
<thead>
<tr>
<th>Type of alumina substrate</th>
<th>Porosity (%)</th>
<th>Average pore diameter (Å)</th>
<th>Thickness of substrate (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-1</td>
<td>0.338</td>
<td>22.1</td>
<td>0.63</td>
</tr>
<tr>
<td>A-2</td>
<td>0.384</td>
<td>51.3</td>
<td>0.54</td>
</tr>
<tr>
<td>A-3</td>
<td>0.762</td>
<td>54.6</td>
<td>0.56</td>
</tr>
</tbody>
</table>

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Fig. 2. Current response on Au/A-3 porous alumina substrate/Pt assembly with step changes of various VCM concentrations. The positions of the arrows indicate the step changes of the indicated concentration of VCM from 0. Applied potential: –2.1 V (vs. Ag/Ag\(^+\)), supporting electrolyte: 10 mM Bu\(_4\)NClO\(_4\).
supporting electrolyte on the sensitivity of vinyl chloride
sensing. Figure 4 shows the sensing current of Au/A-3 porous
alumina plate/Pt assembly for the concentration
range of 0.5 ± 3% at applied potential /C0 2.1 V (vs. Ag/Ag
in 50% toluene/50% DMF electrolyte with two different
supporting electrolytes. The sensitivities for tetrabutylam-
onium perchlorate and tetrabutylammonium tetrafluoborate
were 70.9 and 49.6 /C109 A%/C0 1, respectively. The sensitivity
with tetrabutylammonium perchlorate was 1.43 times as
large as that with tetrabutylammonium tetrafluoborate. In a
similar experiment, the sensitivity of tetrabutylammonium
perchlorate was even 2.98 times as large as that in
tetrabutylammonium tetrafluoborate at applied potential
/C0 2.0 V (vs. Ag/Ag
), as revealed in Table 2. This effect of
supporting electrolyte on the sensitivity might be contrib-
uted to the effect of double layer on the sensing electrode.
Anion of the supporting electrolyte was specifically adsor-
bbed in the double layer and formed the inner Helmholtz
layer, a mono-molecular layer of adsorbed ion. Different
anion created different characteristics of double layer and
could have profound effects on the rate of electron transfer
[20].

3.4. Effect of Applied Potential
The effect of applied potential on the sensitivity for cathodic
reaction of vinyl chloride is depicted in Figure 5. When the
applied potential changed from −1.8 to −2.2 V (vs. Ag/Ag
),
the sensitivity increased from 28.4 to 204 /C109 A%
, concentration of supporting electrolyte: 10 mM.

Table 2. The background current and sensitivity of various types
of alumina substrates and supporting electrolyte. Applied potential:
−2.0 V (vs. Ag/Ag
), concentration of supporting electrolyte: 10 mM.

| Type of | Porosity (%) | Supporting | Background | Sensitivity |
| alumina | | electrolyte | current (µA) | (µA%/%) |
| substrate | | | | |
| A-1 | 0.338 | Bu4NClO4 | 28 | 5.0 |
| A-2 | 0.384 | Bu4NClO4 | 133 | 36.0 |
| A-3 | 0.762 | Bu4NClO4 | 415 | 57.5 |
| A-3 | 0.762 | Bu4NBF4 | 391 | 19.3 |

supporting electrolyte on the sensitivity of vinyl chloride
sensing. Figure 4 shows the sensing current of Au/A-3 porous
alumina plate/Pt assembly for the concentration
range of 0.5–3% at applied potential −2.1 V (vs. Ag/Ag
) in 50% toluene/50% DMF electrolyte with two different

Electroanalysis 2002, 14, No. 17
mainly affected by the kinetic reaction, instead of diffusion.

3.5. Effect of Supporting Electrolyte Concentration

Figure 6 shows the relationship between the sensitivity of cathodic reduction of VCM at applied potentials a) \(-2.0\) and b) \(-2.1\) V (vs. Ag/Ag⁺). Electrode assembly: Au/A-3 porous alumina substrate/Pt, supporting electrolyte: Bu₄NClO₄.

\[
\text{Sensitivity, } \mu\text{A/V}\text{s}^{-1} \quad \text{[but],NCIO}_4, \text{mM}
\]

![Graph showing the relationship between sensitivity and electrolyte concentration.]

The curves marked with triangles and squares are for applied potentials \(-2.0\) and \(-2.1\) V (vs. Ag/Ag⁺), respectively. The sensitivities at \(-2.1\) V (vs. Ag/Ag⁺) were larger than those at \(-2.0\) V (vs. Ag/Ag⁺) in the whole concentration range, 0.1 – 50 mM. At both potentials, the concentration close to 10 mM had the highest sensitivities. For the concentration smaller than 10 mM, the sensitivity increased with the concentration of supporting electrolyte due to decrease of ohmic resistance in the electrolyte. In other words, the conductivity in the electrolyte increased significantly with the concentration of supporting electrolyte and therefore enhanced the cathodic reaction of vinyl chloride. On the other hand, for the concentration larger than 10 mM, the sensitivity decreased when the supporting electrolyte concentration increased because diffusion coefficient of proton, necessary for vinyl chloride reduction [10], decreased. The previous study revealed that the diffusion coefficient of electroactive species decreased with the concentration of supporting electrolyte due to increase of viscosity of the electrolyte [3]. The effect of proton diffusion should be taken into consideration in VCM sensing.

3.6. Effect of Porous Alumina Plate

Three types of porous alumina plates with different porosities were employed as the substrates of the Au/

![Graph showing the relationship between sensing current and VCM concentration.]

Three types of porous alumina plates with different porosities were employed as the substrates of the Au/porous alumina plate/Pt assembly for the vinyl chloride detector. Figure 7 shows the effect of the type of alumina plate on the relationship between the sensing current and the concentration of vinyl chloride at applied potential \(-2.0\) V (vs. Ag/Ag⁺). The curves with the symbols of square, triangle, and circle represent the sensing results for A-1, A-2, and A-3 alumina plates, respectively. They show good linearity with correlation coefficient at least 0.97 in the concentration range of 1.25 ± 4%. The slopes, namely the sensitivities for vinyl chloride gas, of the curves were 5.0, 36.0, and 57.5 \(\mu\text{A} \cdot \text{V}^{-1}\text{cm}^{-2}\) for A-1, A-2, and A-3 porous alumina plates, respectively. The porosities of A-1, A-2, and A-3 alumina plates were 0.338, 0.384, and 0.762%, respectively, in terms of volume ratio of the pore and bulk. Obviously, the sensitivity of cathodic reduction of vinyl chloride increased with the porosity of alumina plate.

![Graph showing the effect of porosity on sensitivity and response time.]

The sensitivities and response times for the assemblies with three types of alumina plates are plotted as functions of the porosity of porous alumina plates, as shown in Figure 8. The response times were recorded with 1.25% VCM/N₂. According to the results in Figure 8, the sensitivity...
increased, and the response time decreased, when the porosity increased. It was believed that the dependence of sensitivity on the porosity was related to the number of three-phase reacting sites for reaction on the surface of the sensing electrode. The number of three-phase reacting sites on the sensing electrode was believed to increase with the coverage of electrolyte. This number reached a maximum at an optimum coverage, beyond which, the number of three-phase reacting sites decreased due to flooding. In the sensing assemblies in this present study, the porosities of the porous alumina substrates were so small that the electrolyte could not reach the optimum coverage of electrolyte. In the sensing assembly with more porous alumina plate, the electrolyte was, therefore, easier to permeate through the alumina substrate and formed larger number of three-phase reacting sites. Greater number of available three-phase reacting sites for reduction of VCM increased the sensing current and thus gave higher sensitivity.

Meanwhile, the background currents for the assemblies with different porosities were observed. The background currents increased with the porosity, as shown in Table 2. The background currents were around 28, 133, and 415 μA for porosities of 0.338, 0.384, and 0.762%. In general, background current increases with the surface area covered by the electrolyte, i.e. the reaction surface area. Therefore, larger background current was expected for the electrode with higher coverage of electrolyte, which was a positive correlation of porosity of the porous alumina plate.

4. Conclusions

In the present study, the sensing behavior of vinyl chloride was investigated at several operating conditions in the concentration range of 0.5–4%. Compared with tetrabutylammonium tetrafluoborate, higher sensitivities were obtained when tetrabutylammonium perchlorate was used as the supporting electrolyte at both the applied potentials, −2.0 and −2.1 V (vs. Ag/Ag⁺). The optimum concentration of tetrabutylammonium perchlorate for the highest sensitivity at −2.0 and −2.1 V (vs. Ag/Ag⁺) was found close to 10 mM in the investigated concentration range, 0.1 – 50 mM. In 50% toluene/50% DMF electrolyte containing 10 mM Bu₄NClO₄, the highest sensitivity of 70.9 μA %⁻¹ in the concentration range of 0.5–3% was obtained at −2.1 V (vs. Ag/Ag⁺). This sensitivity was around 37 times as large as that in the concentration range of 13–44.5% in our previous works. One of the contributions was from the larger porosity of porous alumina substrate. The sensing current and the sensitivity of vinyl chloride sensing was increased significantly with the porosity of the porous alumina substrate.

5. Acknowledgements

Financial support from National Science Council (NSC-89-EPA-Z-006-003), National Cheng Kung University, and Environmental Protection Administration in Taiwan are gratefully acknowledged. The authors also thank Leatec Fine Ceramics Co. for the special provision of porous alumina substrate.

6. References