A Study on Monitoring of Vinyl Chloride Gas by an Indirect Sensing Method

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An indirect sensing method is described for vinyl chloride with an amperometric sensor connected to a prepyrolysis column. Significant sensing ability to the pyrolyzed gas, produced from pyrolysis of 0–30 ppm vinyl chloride gas, was obtained with a Pt/porous alumina substrate assembly. Furthermore, the sensing current was proportional to the concentration of vinyl chloride gas in the investigated concentration range. The sensitivity and sensing limit for vinyl chloride were observed as functions of pyrolysis temperature, gas flow rate, and applied potential. Preferable sensing parameters were 400°C, 150 mL min⁻¹, and 1.2 V (vs. Ag/AgCl), in which the sensing reaction was controlled by gas diffusion. Effect of porosity of porous alumina substrate on the sensing performances was also studied. The electroactive species, which was contained in the pyrolyzed gas and electrochemically oxidized on the sensing electrode, was suggested to be hydrogen chloride vapor.

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Halogen-containing compounds have been extensively used in industries. Vinyl chloride, the monomer for production of poly(vinyl chloride), has been used for several decades. The total global production capacity of vinyl chloride monomer (VCM) was expected to reach 33.01 million tons in 2003. Nevertheless, the characteristics of vinyl chloride, including high flammability, carcinogenicity, and damage to the liver, blood vessels, and connective tissue, have been confirmed. Approximate 4% loss estimate of VCM has been reported, based primarily on material balance studies. Detectors are necessary to monitor the loss from industrial sources in order to avoid the damages to humans and the environment.

The conventional solid polymer electrolyte (SPE), e.g., Nafion, has been commonly used to fabricate amperometric gas sensors since 1970s. Other assemblies used porous Teflon membrane or porous alumina substrate (SPE) to replace Nafion with a similar function. These two assemblies allowed the penetration of electrolyte from the electrolyte chamber to the surface of sensing electrode, and provided triple-phase reacting sites for electrochemical reactions of gaseous compounds.

Several kinds of assemblies with metal electrodes deposited on SPE have been developed to measure the concentrations of organic reducing gases. Nevertheless, the assemblies were generally not very suitable to analyze oxidative organic compounds at very negative potential due to considerable water electrolysis. This problem can be solved by replacing the aqueous electrolyte with a nonaqueous electrolyte that is difficult to reduce and is sufficiently stable in electrochemical reaction. Widely accessible potential range made some oxidizing electroactive gases, e.g., carbon dioxide, nitrogen dioxide, and vinyl chloride electrochemically analyzable. However, a crucial effect of moisture on the sensing behavior was usually observed. This effect became substantial when the concentration of electroactive species was smaller than the concentration of moisture, and restricted the development of sensors toward lower sensing limit by direct sensing method.

An indirect detecting method has been applied to determine the concentration of electrochemically weak- or in-active species via monitoring one of the pyrolysis products. Sample gas was exposed to a heated platinum or gold filament before being introduced into the gas chamber of amperometric sensors. Lead phthalocyanine (PbPc) film was also used to determine chlorinated hydrocarbon by monitoring the concentration of chlorine, produced by decomposition of the chlorinated hydrocarbons over a heated platinum coil.

Investigations in the combustion and pyrolysis of chlorinated hydrocarbons have been carried out due to an environmental concern. Hydrogen chloride was one of the pyrolysis products from chlorinated compounds. Vinyl chloride began to thermally decompose at the pyrolysis temperature above 450°C to form a small amount of acetylene and by-products.

An amperometric detector for vinyl chloride with the concentration range of 0.5–45% has been developed with an Au/PAS electrode assembly in nonaqueous electrolytes. The detection of vinyl chloride toward lower concentration by the direct sensing mode was difficult due to the significant effect of interfering species. To solve this problem, monitoring of vinyl chloride in nitrogen atmosphere at the concentration range of parts per million was, therefore, approached with a prepyrolysis method in this study. For sakes of high conversion on pyrolysis and uniform temperature distribution, a pyrolysis column, instead of the heated metal filament, was applied. The effects of applied potential, flow rate, pyrolysis temperature, and porosity of substrate on the sensing performances were studied. The electroactive species in the pyrolytic product was also identified.

Experimental

Pyrolysis and testing apparatus.—A combination system of VCM pyrolysis and electrochemical sensing is shown in Fig. 1. Test gas with desired concentration of VCM was prepared with a mixing device (A) by blending 1000 ppm vinyl chloride gas (Scott Specialty Gases) with highly pure nitrogen (99.99%). The flow rate was controlled with two mass flow controllers (FC-2901, Millipore). The test gas (VCM/N₂) was then transported through a pyrolysis column (C), a 316 stainless steel tube with 1/8 in. outer diameter and 4 m in length. The pyrolysis column was shaped into a coil of 4 in. diam and mounted in a furnace (D) (RHDH-30, Risen). Vinyl chloride was pyrolyzed in the heated column at a temperature below 500°C regulated by a temperature controller (SR-T7, CAHO). One fire arrester (B) (6104, Matheson) was installed before the inlet of pyrolysis column in order to avoid flashback. After pyrolysis, the pyrolytic product was then transported to one electrochemical sensing cell (F). Before being vented into the air, the outlet gas from the cell passed through an absorption column (G) filled with calcium hydroxide powder (95%, Showa).

The residence time (τ) in the pyrolysis column was calculated according to
Measurements of sensing current and porosity of alumina plate.—Chronoamperometric experiments were applied to determine the current response with a potentiostat (614A, CHI). The sensing current was calculated from the difference between the background current in pure N\textsubscript{2} atmosphere and the measured current in VCM/N\textsubscript{2}. The pore volumes of the two types of PAS (Leatee Fire Ceramics Co., Taiwan) 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 and 10\textsuperscript{−3} Torr. The total volume were determined at \(p/p_0 = 0.99\). The porosities for types A-2 and A-3 PAS were 0.384 and 0.762%, respectively, in terms of ratio of pore volume to bulk volume.

Gas chromatography analysis.—As shown in Fig. 1, the pyrolytic product for analysis was collected with a syringe (E) at the effluence of pyrolysis column. The sampling volume was 1 mL. A gas chromatography (GC-14A, Shimadzu) with a 30 m long capillary column (DB-5, J&W Scientific) was used to determine the composition of pyrolyzed gas. The temperatures of capillary column, injector, and flame ionization detector were 50, 150, and 250°C, respectively.

Analysis of HCl.—The pyrolyzed gas was bubbled through one absorption column containing 39 mM Na\textsubscript{2}SO\textsubscript{4} solution for 30 min. Two milliliters of 0.375 M ferric nitrate (99%, Showa) and 2 mL saturated mercuric thiocyanate (99%, Janssen) in ethanol was added into a 20 mL absorption solution. The absorbance of absorption solution against a blank reagent at 463 nm was determined by a UV visible spectrometer (UV-160A, Shimadzu). The detailed procedure of the analysis was described previously.

Analysis of chlorine.—The pyrolyzed gas was bubbled through an absorption column containing 0.1 M KI (99.8%, Katayama) for 30 min. The absorbance of the absorption solution was measured with UV/vis spectrometer in the wavelength range of 200–800 nm against a reagent of 0.1 M KI containing 0.1 mM I\textsubscript{2} (99.8%, Showa).

Results and Discussion

Determination of pyrolysis parameters.—For the same length of pyrolysis column, the conversion of vinyl chloride by thermodecomposition was suggested to be influenced by (1) concentration of vinyl chloride, (2) gas flow rate, and (3) pyrolysis temperature. Analysis of the pyrolytic product was carried out by gas chromatography (GC) to find the appropriate pyrolysis condition in which the vinyl chloride gas was thermo-decomposed completely. Figure 3 shows the GC spectra of 1000 ppm vinyl chloride gas without pyrolysis, as well as 30 ppm vinyl chloride gas with pyrolysis temperatures of 250 (c), 300 (d), and 400°C (e) at the gas flow rate of 150 mL min\textsuperscript{−1}. The peak at residue time of 2.3 min was specified for vinyl chloride. When the pyrolysis temperature increased, the peak area of vinyl chloride decreased and vanished at the pyrolysis temperature of 400°C. Namely, at a pyrolysis temperature of 400°C and flow rate of 150 mL min\textsuperscript{−1}, 30 ppm vinyl chloride could be thermodecomposed completely.

The minimum pyrolysis temperatures for lower concentration of vinyl chloride and lower flow rate were investigated also. Generally, the necessary minimum pyrolysis temperature for complete vinyl chloride decomposition increased with vinyl chloride concentration and gas flow rate. The pyrolysis temperature of 400°C was confirmed to be enough for vinyl chloride decomposition under the

where \(v\), \(D\), and \(L\) are volumetric flow rate of gas, inside diameter of pyrolysis column, and length of pyrolysis column, respectively. The residence time at flow rate of 150 mL min\textsuperscript{−1} was around 1.8 s.

Electrochemical sensing cell.—The electrochemical sensing cell used in the present study has been described previously, as shown in Fig. 2. It consisted of a porous alumina substrate (PAS) (A) with a Pt sensing electrode (B) on one side, a coiled platinum wire (C) as the counter electrode, an Ag/AgCl reference electrode in 3 N KCl solution (D), and two chambers filled with 0.5 M H\textsubscript{2}SO\textsubscript{4} electrolyte (E) and testing gas (F), separately. A platinum sensing electrode was prepared by sputtering under 0.1 mbar argon (99.999%) atmosphere with a sputter coater (K550x, Emitech). One shadow mask, made of poly(methyl methacrylate) plate, was used to form the electrode pattern during sputtering process. The sputtering conditions were 40 mA dc for 16 min. The geometric area and the thickness of the sensing electrode were 1.76 cm\textsuperscript{2} and 200 nm, respectively. One silver-coated lead wire, 0.3 mm in diameter, was connected to the electrode with Ag paste. Two gaskets (G) were used to prevent leakage of test gas and electrolyte from the gas and electrolyte chambers, respectively. In this assembly, the electrolyte permeated through the PAS 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, available to exert the anodic reaction of electroactive species, were the junction of the test gas (gas phase), the electrolyte (liquid phase), and the sensing electrode (solid phase).
investigated flow rate: 0–150 mL min⁻¹, and concentration, 0–30 ppm, in this study.

**Response curve.**—After pyrolysis of vinyl chloride at 400°C, the current response of Pt/A-2 PAS electrode assembly at 1.3 V vs. Ag/AgCl for pyrolyzed gas, produced from various concentrations of vinyl chloride, is shown in Fig. 4. The Pt sensing electrode was exposed to the test gases with the concentration of vinyl chloride changing from 5 to 30 ppm at an interval of 5 ppm successively after a steady-state background current was obtained. Obviously, the responding current increased with the concentration of vinyl chloride and finally decreased when the subjected gas was changed to pure nitrogen. The response time, the time to reach steady state current, for each concentration change was within 12 min except that at 10 ppm. A linear relationship, with a correlation coefficient of 0.999, between the sensing current and the concentration of vinyl chloride is depicted as an insert in Fig. 4. The Pt sensing electrode was Ag/AgCl for pyrolyzed gas, produced from various concentrations of vinyl chloride concentration. On the other hand, the sensing limit at the flow rate of 150 mL min⁻¹ had the minimum sensing limits among the three potentials. On the other hand, the sensing limit at the flow rate of 150 mL min⁻¹, 1.2 V had the minimum sensing limits among the three potentials. On the other hand, the sensing limit at the flow rate of 150 mL min⁻¹ increased slightly when the applied potential was more positive. Obviously, the sensing limit in the flow rates of 50 and 100 mL min⁻¹ were more dependent on the applied potential than that in 150 mL min⁻¹.

The sensitivity of sensing limit on the applied potential is shown in Table I. At the flow rates of 50 and 100 mL min⁻¹, 1.2 V had the minimum sensing limits among the three potentials. On the other hand, the sensing limit at the flow rate of 150 mL min⁻¹ increased slightly when the applied potential was more positive. Obviously, the sensing limit in the flow rates of 50 and 100 mL min⁻¹ were more dependent on the applied potential than that in 150 mL min⁻¹.

The effect of applied potential on the sensitivity of vinyl chloride under various flow rates was illustrated in Fig. 5. At the flow rates of 100 and 150 mL min⁻¹, the sensitivity increased when the applied potential changed from 1.0 to 1.2 V, and became rather constant between 1.2 and 1.3 V. These two flow rates gave consistent sensitivity at 1.0 and 1.1 V, but significant difference at more positive potentials. It implied that the reaction rate at 1.1 V or less positive than 1.3 V were not suitable for detection of pyrolyzed gas due to an obscure sensing signal or the small ratio of sensing current/background current, respectively. The applied potentials between 1.1 and 1.3 V were, therefore, applied to investigate the effect of potential on both the sensitivity and sensing limit.

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tively anodic oxidation between the electroactive species and water on the sensing electrode. Therefore, both too large and too small overpotentials diminished the detecting capability toward low concentration, and thus had larger sensing limits. The applied potential of 1.2 V was preferred for detection of pyrolyzed gas because of its smaller sensing limit, larger sensitivity, and moderate background current. Furthermore, under this potential at 150 mL min\(^{-1}\) gas flow rate, the sensing limit was calculated as 2.0 ppm based on three times of standard deviation of response currents.

Effect of flow rate.—Figure 6 shows the effect of flow rate on the sensitivity of vinyl chloride at different applied potentials. The sensitivities at 1.2 and 1.3 V increased from 1.87 to 6.73 \(\mu\)A ppm\(^{-1}\) and from 2.37 to 6.73 \(\mu\)A ppm\(^{-1}\), respectively, when the flow rate increased from 50 to 150 mL min\(^{-1}\). It was believed that larger flow rate reduced the thickness of diffusion layer, decreased the diffusion resistance, and thus increased the sensitivity. The sensitivity at 1.1 V also increased with the flow rate but reached a constant value since the kinetic reaction became the rate-determining step.

In addition, the sensing limit as a function of flow rate is also illustrated in Table I. The gas flow over the electrode may uptake electrolyte from the electrode surface. A low gas flow rate was supposed to produce high electrolyte coverage on the surface of sensing electrode if no flooding occurred. Either high or low electrolyte coverage yielded a small no. of triple-phase reacting sites on the electrode. This phenomenon was usually observed in the research of fuel cells.\(^{24}\) There was a maximum number of triple-phase reacting sites, with a minimum kinetic resistance, at an optimum electrolyte coverage and gas flow rate. The gas flow rates in this study were believed to be smaller than the optimum flow rate. Namely, the flow rate of 150 mL min\(^{-1}\) had the maximum number of triple-phase reacting sites, resulting into the lowest sensing limit. Additional, the sensing process at 1.2 or 1.3 V in 50 mL min\(^{-1}\) was not certainly controlled by diffusion (refer Fig. 5), even though those in the larger flow rates were diffusion controlled. It was believed that reactions at the flow rate of 50 mL min\(^{-1}\) in the potential range of 1.1--1.3 V were controlled by both diffusion and kinetic reaction since the kinetic resistance at 50 mL min\(^{-1}\) was larger than that at 100 or 150 mL min\(^{-1}\).

Effect of porosity of porous alumina substrate.—Two types of porous alumina plate with different porosity were employed as the substrate of the Pt/PAS assembly electrode for the detection of pyrolyzed gas. Figure 7 shows the effect of the type of alumina substrate on the sensitivity at various applied potentials. The sensitivity for type A-3 PAS increased from 0.1 to 5.79 \(\mu\)A ppm\(^{-1}\) when the applied potential changed from 0.9 to 1.1 V. This strong potential dependence indicated that the sensing process with A-3 substrate was determined by kinetic reaction rather than diffusion. The A-3 PAS, with larger porosity, had smaller penetration resistance of electrolyte through the substrate, and thus gave larger coverage of electrolyte on the electrode surface. As stated previously, the increase in coverage would raise the kinetic resistance, and make the reaction inclined to be kinetic controlled. Similar effects of porosity on the sensing signal was also discussed previously.\(^{1}\) At the applied potential larger than 1.1 V, the background current was larger than 200 \(\mu\)A, and thus was not favorable for the appropriate sensing potential. The larger porosity (type A-3 PAS) not only gave larger background current but also led the appropriate potential to a more negative value (nearly 1.05 V), compared with that in A-2 substrate (1.2 V). This is because of larger coverage of electrolyte on the sensing electrode and smaller ohmic overpotential between sensing and reference electrodes. However, the sensing limits with both A-2 and A-3 types porous alumina substrate at the appropriate applied potentials were about 4 ppm, as shown in Table I.

Effect of pyrolysis temperature.—The sensing performances of Pt/A-2 PAS electrode assembly at the pyrolysis temperature above 300°C are listed in Table II. Both sensitivity and sensing limit at pyrolysis temperatures of 400 and 470°C were almost identical, but not at 300°C. The response curve of PtxA-2 PAS electrode assembly

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**Table I. Sensing limit as a function of flow rate, applied potential, and types of PAS.**

<table>
<thead>
<tr>
<th>Type of PAS</th>
<th>Flow rate (mL min(^{-1}))</th>
<th>Applied potential (V vs. Ag/AgCl)</th>
<th>Sensing limit(^a) (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-2</td>
<td>50</td>
<td>1.1</td>
<td>11.8</td>
</tr>
<tr>
<td>A-2</td>
<td>50</td>
<td>1.2</td>
<td>7.7</td>
</tr>
<tr>
<td>A-2</td>
<td>50</td>
<td>1.3</td>
<td>13.4</td>
</tr>
<tr>
<td>A-2</td>
<td>100</td>
<td>1.1</td>
<td>8.9</td>
</tr>
<tr>
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<td>100</td>
<td>1.2</td>
<td>3.9</td>
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<tr>
<td>A-2</td>
<td>100</td>
<td>1.3</td>
<td>8.9</td>
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<tr>
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<td>150</td>
<td>1.1</td>
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<tr>
<td>A-2</td>
<td>150</td>
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<tr>
<td>A-3</td>
<td>100</td>
<td>1.0</td>
<td>4.3</td>
</tr>
<tr>
<td>A-3</td>
<td>100</td>
<td>1.1</td>
<td>8.1</td>
</tr>
</tbody>
</table>

\(^a\) Pyrolysis temperature: 400°C.

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**Figure 6.** Relationship between sensitivity and gas flow rate at various applied potentials with Pt/A-2 PAS electrode assembly. Pyrolysis temperature: 400°C.

**Figure 7.** Dependence of sensitivity on the applied potential at two porous alumina substrates. Gas flow rate: 100 mL min\(^{-1}\), pyrolysis temperature: 400°C.
for various concentrations of vinyl chloride at pyrolysis temperature of 300°C is shown in Fig. 8. The sample gas with 5 ppm vinyl chloride was found not detectable. The responding current increased when concentration of vinyl chloride changed from 10 to 20 ppm but decreased for higher concentration, 25 ppm. This behavior was explained that the vinyl chloride gas with the concentrations below 20 ppm could be thermally decomposed completely at 300°C; whereas not for higher concentration. It also could be confirmed from the GC spectrum, as shown in Fig. 3d. The peak for residue of vinyl chloride was still observed after pyrolysis at 300°C. The incomplete decomposition made the responding current not increase subsequently with the vinyl chloride concentration. However, the phenomenon that the responding current decreased for concentration above 20 ppm, instead of staying a consistent value, would be further investigated.

**Electroactive species for indirect sensing mode.** —The composition of pyrolyzed gas, especially the electroactive species that was electrochemically oxidized on Pt sensing electrode, should be identified. The electroactive species for pyrolysis of a variety of hydrocarbons/air via a heated platinum filament was proposed to be carbon monoxide by Stetter et al.\textsuperscript{14-17} However, the electroactive species in this study should not be carbon monoxide due to absence of oxygen. Other previous study\textsuperscript{22} indicated that vinyl chloride was thermally decomposed at pyrolysis temperature above 450°C to form a small amount of acetylene and by-products. The pyrolytic products in this study were, therefore, suggested to be four possible compounds: acetylene, hydrogen chloride, chlorine, and unknown hydrocarbons. Each of them was searched and are described below.

**Acetylene.**—Acetylene or other hydrocarbons were identified by GC. Nevertheless, no peak for C\textsubscript{2}H\textsubscript{2} or other hydrocarbons was observed in the spectrum of pyrolyzed gas within 30 min of residue time. It indicated that either C\textsubscript{2}H\textsubscript{2} was absent in the pyrolyzed gas or the concentration of C\textsubscript{2}H\textsubscript{2} was too low to be detected by the flame ionization detector. A direct verification was also performed. The Pt/A-2 PAS electrode assembly attempted to detect 30 ppm C\textsubscript{2}H\textsubscript{2} with the response curve as shown in Fig. 9a. No sensing current was obtained when the subjected gas changed from N\textsubscript{2} to C\textsubscript{2}H\textsubscript{2} gas at the time of the 36th min. That meant acetylene should be excluded from the electroactive species to be electrochemical oxidized on the sensing electrode.

**Chlorine.**—If chlorine were contained in the pyrolyzed gas, chlorine reacted with KI to form potassium chloride and iodine, which could be analyzed by a colorimetric method

\[
\text{KI} + \text{Cl}_2 \rightarrow \text{KCl} + \text{I}_2
\]

After the pyrolyzed gas was absorbed with 0.1 M KI solution, the spectrum of absorption solution was obtained and shown in Fig. 10a. A low concentration, 0.1 mM, of I\textsubscript{2} solution was used to provide a reasonable comparison. The spectrum of pyrolyzed gas absorbed solution did not show the two peaks at 285 and 350 nm, which appeared in the solution in the presence of I\textsubscript{2} as curve (b). This result confirmed that chlorine was absent in the pyrolyzed gas.

\begin{table}
\centering
\begin{tabular}{|c|c|c|}
\hline
Pyrolysis temp. \(^a\) (°C) & Sensitivity (\(\mu\text{A} \text{ ppm}^{-1}\)) & Sensing limit (ppm) \\
\hline
470 & 6.80 & 3.6 \\
400 & 6.87 & 3.8 \\
300 & \(\cdots\) & >5 \\
\hline
\end{tabular}
\end{table}

\(^a\) Applied potential: 1.2 V (vs. Ag/AgCl). Gas flow rate: 150 mL min\textsuperscript{-1}.
and would not be the electroactive species. Furthermore, chlorine is likely to be electrochemically reduced rather than oxidized.

**Hydrogen chloride.**—HCl, involved in the pyrolyzed gas, was analyzed qualitatively by spectrometry. Figure 10c and d show the UV/vis spectra of 39 mM NaOH solution before and after absorption of pyrolyzed gas, respectively. The absorbance, at wavelength of 463 nm, increased from 0.082 to 0.104 after absorption. It indicated that small amount of HCl was definitely present in the pyrolyzed gas and could be less positive. The electroactive species, which was contained in the analyzed gas, was suggested to be hydrogen chloride vapor.

A hydrogen chloride vapor was prepared by purging nitrogen through one column containing 6 M concentrated HCl solution and was detected by the Pt/A-2 PAS electrode assembly. The response curve at 1.2 V is shown in Fig. 9b. A significant responding current was detected by the Pt/A-2 PAS electrode assembly. The response activity, i.e., vinyl chloride gas, was not electrochemical analyzable with a direct sensing method. Under pyrolysis temperature of 400°C, gas flow rate of 150 mL min⁻¹, and applied potential of 1.2 V (vs. Ag/AgCl), the sensitivity and sensing limit were 6.87 µA ppm⁻¹ and 3.8 ppm, respectively. The sensitivity and sensing limit at pyrolysis temperature of 470°C was consistent with those at 400°C but with a deviation at 300°C due to incomplete decomposition of vinyl chloride. The sensing processes in the flow rates both 100 and 150 mL min⁻¹ were suggested to be controlled by gas diffusion at applied potentials more positive than 1.2 V (vs. Ag/AgCl), yet by kinetics at 1.1 V (vs. Ag/AgCl). Furthermore, both diffusion and kinetic steps were important in the sensing processes at potentials from 1.1 to 1.3 V (vs. Ag/AgCl) in gas flow rate of 50 mL min⁻¹. Larger porosity of PAS not only increased the background current but also shifted the appropriate sensing potential to be less positive. The electroactive species, which was contained in the pyrolyzed gas and electrochemically oxidized on the sensing electrode, was suggested to be hydrogen chloride vapor.

**Conclusions**

Vinyl chloride gas in the concentration range of 0–30 ppm was detected with a Pt/PAS electrode assembly by an indirect method. It resolved the problem, which the species with poor electrochemical activity, i.e., vinyl chloride gas, was not electrochemical analyzable with a direct sensing method. Under pyrolysis temperature of 400°C, gas flow rate of 50 mL min⁻¹, and applied potential of 1.2 V (vs. Ag/AgCl), the sensitivity and sensing limit were 4.87 µA ppm⁻¹ and 3.8 ppm, respectively. The sensitivity and sensing limit at pyrolysis temperature of 470°C was consistent with those at 400°C but with a deviation at 300°C due to incomplete decomposition of vinyl chloride. The sensing processes in the flow rates both 100 and 150 mL min⁻¹ were suggested to be controlled by gas diffusion at applied potentials more positive than 1.2 V (vs. Ag/AgCl), yet by kinetics at 1.1 V (vs. Ag/AgCl). Furthermore, both diffusion and kinetic steps were important in the sensing processes at potentials from 1.1 to 1.3 V (vs. Ag/AgCl) in gas flow rate of 50 mL min⁻¹. Larger porosity of PAS not only increased the background current but also shifted the appropriate sensing potential to be less positive. The electroactive species, which was contained in the pyrolyzed gas and electrochemically oxidized on the sensing electrode, was suggested to be hydrogen chloride vapor.

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