Explosive gas recognition system using thick film sensor array and neural network

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Abstract

A sensor array with nine discrete sensors integrated on a substrate was developed for recognizing the species and quantity of explosive gases such as methane, propane, and butane. The sensor array consisted of nine oxide semiconductor gas-sensing materials with SnO₂ as the base material plus a heating element based on a meandered platinum layer all deposited on the sensor. The sensors on the sensor array were designed to produce a uniform thermal distribution and show a high and broad sensitivity and reproducibility to low concentrations through the use of nano-sized sensing materials with high surface areas and different additives. Using the sensitivity signals of the array along with an artificial neural network, a gas recognition system was then implemented for the classification and identification of explosive gases. The characteristics of the multi-dimensional sensor signals obtained from the nine sensors were analyzed using the principal component analysis (PCA) technique, and a gas pattern recognizer was implemented using a multi-layer neural network with an error back propagation learning algorithm. The simulation and experimental results demonstrate that the proposed gas recognition system is effective in identifying explosive gases. For real time processing, a DSP board (TMS320C31) was then used to implement the proposed gas recognition system in conjunction with a neural network.

Keywords: Tin oxide; Sensor array; Explosive gases; Neural network

1. Introduction

Recently, as the usage of LNG and LPG gas has increased, the frequency of accidental explosions due to leakage has sharply increased. The ability to detect and precisely measure gas leakage is crucial in preventing the occurrence of such accidents. Accordingly, the development of sensors and systems that can selectively detect and determine the quantity of specific gases below the explosion limit, in situ, is urgently needed. Until now, there have been various reports on the use of different kinds of metal oxide sensors for detecting explosive hydrocarbon gases, which have offered many improvements from the perspective of stability [1]. Furthermore, to overcome the poor selectivity and long-term drift of a sensor signal, studies have also been conducted to develop an electronic nose with sensor array systems consisting of various sensing materials such as metal oxides, electrochemical sensors, conducting polymers, field effect transistor devices, surface acoustic wave devices, and hybrid sensor arrays [2–11].

For continuous use, without relearning, an electronic nose requires high reliability, stability, and sensitivity from the individual sensors that make up the nose. However, sensor responses tend to drift significantly when sensors are used over a long period of time resulting in poor selectivity and redundant pattern recognition. Therefore, the fabrication of more reliable and stable sensors, or the ability to adjust the pattern recognition routine according to variations in the sensor response is needed. Accordingly, nano-sized tin oxide materials were synthesized using the coprecipitation method and nine kinds of highly sensitive and stable thick film sensors were fabricated on a substrate. Using the sensitivity signals of the arrays and an artificial neural network, a gas pattern recognition was then implemented using a DSP (TMS320C31) board with the aim of classifying and quantifying specific explosive gases, including butane, propane, and methane below their explosion limit value.
2. Experimental

2.1. Preparation of base material

The priority for the reliable recognition of leaked explosive gases is the development of stable individual sensors that exhibit a high sensitivity to gases. Therefore, sensing materials that can satisfy the above conditions need to be fabricated and processed. It has been previously reported that reducing particles to a nano-size through the addition of Ca along with the spillover effect caused by adding the Pt catalyst enhances the sensitivity of sensing materials to gases even at low concentrations [12].

For preparing the raw materials, a solution containing SnCl₄, (CH₃CO₂)₂Ca·xH₂O and, H₂PtCl₆·6H₂O was coprecipitated by controlling the pH value while dropping a NH₄OH solution to a white precipitated powder. The powder was then washed with an NH₄NO₃ solution for 3 days, dried in an oven at 100°C for 24 h, and calcined in an electric furnace at 600°C for 1 h. The Ca and Pt contents were both set at 0.1 wt.% relative to the amount of SnCl₄. Using this powder as a base material, nine kinds of sensing materials with different additives such as Pd, Au, Pt, CuO, La₂O₃, Sc₂O₃, TiO₂,WO₃, and ZnO within a range of 0.1–5 wt.% were evenly mixed by hand-milling for 1 h to modify the selectivity spectrum of the sensors. A process chart for the base material is shown in Fig. 1. The selection of the additives for the sensor array was based on previously reported results [12–16].

2.2. Fabrication of sensor array and measurement

The sensor array consisting of nine metal-oxide semiconductor gas sensors along with their dopants is shown in Table 1. The coprecipitated SnO₂/Ca,Pt (0.1 wt.%) powder was used as the base material. The sensing films were all prepared using the silk printing technique. After being simultaneously deposited by the silk printing method, the sensing films were then annealed at 800°C for 2 h in air. The following presents a brief outline of the results produced by the sensors on the array listed in Table 1. All the sensing materials were deposited on an alumina substrate (55 m x 14 m) along with a heating element and temperature sensor based on a meandered silk-printed platinum layer on the backside of the substrate. Platinum pads and interdigitated platinum contacts were deposited on the front-face of the substrate.

As shown in Fig. 2, the sensor array was connected with the long bonding pins for electrical conduction and thermal isolation from the socket and peripheral circuit. The characteristics of the sensor array were then tested in a testing chamber after injection of explosive gases of butane, propane, and methane at 400°C. The sensor signals were transferred to a test system and monitored using a personal computer in a testing chamber, as shown in Fig. 3.

The microstructure of the basic sensing-film was investigated using transmission electron microscope (TEM), X-ray diffraction (XRD), and Brunauer-Emmett-Teller (BET) adsorption, and a voltage detecting method was used to calculate the sensitivity of the sensor [17]. The sensitivity was defined as \( R_{\text{air}} - R_{\text{gas}} / R_{\text{air}} \times 100 \% \), where \( R_{\text{gas}} \) and \( R_{\text{air}} \) are the electrical resistances in explosive gas and clean air, respectively.

3. Results and discussions

3.1. Analysis of thick films

To selectively determine the quantity of explosive gases below their low explosion limit (methane: 5.3 vol.%, propane: 3.3 vol.%, butane: 1.9 vol.%), stable sensors with a high sensitivity to low concentrations are required. To improve the sensitivity of a sensor, the particle size, specific surface area, and crystalline structure are all recognized as significant parameters [18–20]. Accordingly, the microstructure of various base materials was investigated for its adaptability.

The XRD patterns of calcined SnO₂/Ca,Pt (0.1 wt.%) powders at different annealing temperatures are shown in Fig. 4. This figure indicates higher peak patterns with increased temperatures. All peak patterns observed followed
the rutile structure (JCPDS 21-1250) of the commercial powder (99.9%, Aldrich Co.).

TEM photographs of this powder with and without Ca after being calcined at 600°C for 1 h are shown in Fig. 5. The Ca-added powder exhibited restrained particle growth sizes.

Xu et al. reported that a reduced particle size produces a significant increase in sensitivity [19,20]. Accordingly, the Ca-added powder would be more sensitive in detecting low-level gas concentrations. Based on the above papers, the particle sizes of commercial SnO2, precipitated SnO2, and SnO2/Ca,Pt powders were measured using XRD and TEM analyses, as shown in Table 2. After measuring the full width at half maximum (FWHM) of the XRD pattern peaks, the particle size was then calculated using Scherrer’s formula.

![Fig. 2. Structure of sensor array.](image)

![Fig. 3. Schematic diagram for measuring the properties of sensor array.](image)

![Fig. 4. XRD patterns of SnO2/Ca,Pt (0.1 wt.% powders at varying temperatures.](image)
The differences between the values of the XRD and TEM analyses were due to the pretreatment process for the TEM photographs. The particle size of the precipitated SnO₂ powder was smaller than that of the commercial powder. The particle size of the coprecipitated SnO₂/Ca,Pt powder was the smallest at 7 nm after being calcined at 600 °C for 1 h. Accordingly, it is believed that a sensor with nano-sized powders will be effective in detecting low-level gas concentrations.

Using the BET method, the nitrogen sorption curve for the base material was investigated, as shown in Fig. 6. The hysteresis recorded in the graph indicated a higher number of pores in the sensing materials, which produces more effective gas diffusion and a higher sensitivity. The specific surface areas calculated from this curve are shown in Table 3. As the annealing temperature increased, the specific surface area decreased. The coprecipitation of SnO₂ with Ca and Pt produced an increased specific surface area.

### 3.2. Explosive gas-sensing characteristics of SnO₂-based gas sensors

The response time of a sensor to a gas is directly related to gas detection and classification. Thus, the time response property of the sensor array to objective gases is very important. The time response curve of the sensor array to 4000 ppm propane at 400 °C is shown in Fig. 7. It shows that the gas reaction began to saturate within 3–5 s and desorption of the gas was also completed within 30 s. The detection and recognition of a gas was thus completely finished within 2–3 min, in situ. The sensors also exhibited a variety of sensitivity curves according to the additives used to obtain gas selectivity.

Different sensing patterns for the sensors are critical for conferring selectivity to a sensor array. Fig. 8 shows the

Table 2
Particle size of SnO₂ and SnO₂/Ca,Pt powders for the heating temperature

<table>
<thead>
<tr>
<th>Calcining temperature (°C)</th>
<th>Pure SnO₂ (nm)</th>
<th>Commercial SnO₂ (nm)</th>
<th>0.1 wt.% SnO₂/Ca,Pt (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>XRD  TEM</td>
<td>XRD  TEM</td>
<td>XRD  TEM</td>
</tr>
<tr>
<td>Room temperature</td>
<td>5  5.5</td>
<td>15.8  16.5</td>
<td>2.5  2</td>
</tr>
<tr>
<td>500</td>
<td></td>
<td></td>
<td>5.6  5</td>
</tr>
<tr>
<td>600</td>
<td>9  10</td>
<td>34.8  35</td>
<td>7.2  7.5</td>
</tr>
<tr>
<td>700</td>
<td>15  15.5</td>
<td></td>
<td>10.8  10</td>
</tr>
<tr>
<td>800</td>
<td>20  20</td>
<td></td>
<td>12.1  12.5</td>
</tr>
<tr>
<td>900</td>
<td>24  24.5</td>
<td></td>
<td>17.6  18</td>
</tr>
<tr>
<td>1000</td>
<td>28  29</td>
<td></td>
<td>26.5  27</td>
</tr>
</tbody>
</table>
sensitivity of the sensor array to explosive gases such as butane, propane, and methane below their LELs, specifically at 2000, 4000, and 6000 ppm, respectively. All sensors exhibited a variety of sensitivity ranging from 20 to 100% and showed a monotonous increase of sensitivity with increased gas concentrations. This figure also shows the effects of additives in the base material, that is, sensing materials with the addition of TiO$_2$ showed the highest sensitivity to butane, whereas the addition of TiO$_2$ or ZnO showed the highest sensitivity to propane. The highest sensitivity to methane was shown in sensing materials with the addition of La$_2$O$_3$. Accordingly, it is believed that the use of these patterns will produce distinguishable selectivity in a sensor array.

The sensor responses tend to drift significantly when sensors are used over a long period of time resulting in poor selectivity and redundant pattern recognition. Therefore, the fabrication of more reliable and stable sensors, or the ability to adjust the pattern recognition routine according to variations in the sensor response is needed. For example, Fig. 9 shows the long-term stability of a sensor with nano-sized tin oxide materials, especially SnO$_2$/Ca,Pt (0.1 wt.%) + Pt,Pd (2 wt.%) sensor. The sensor shows long-term stability in air and in 2000 ppm butane for 12 months. But, the sensitivity decreased gradually and slowly. Thus, by employing the conventional pattern recognition routine, we worked on the adjustment to variations in the sensor response.

Table 3
Specific surface area of SnO$_2$ and SnO$_2$/Ca,Pt powders for the heating temperature

<table>
<thead>
<tr>
<th>Condition</th>
<th>SnO$_2$ (m$^2$/g)</th>
<th>SnO$_2$/Ca,Pt (0.1 wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcination at 600°C, 1 h</td>
<td>25.5</td>
<td>35</td>
</tr>
<tr>
<td>Annealing at 800°C, 1 h (after calcination)</td>
<td>19.8</td>
<td>26</td>
</tr>
</tbody>
</table>
The possibility of classifying the species and quantity of a specific gas can be achieved by using a principal component analysis (PCA) that can map multi-dimensional data onto two- or three-dimensional axes with the minimum loss of information [22]. After the data shown in Fig. 8 was remeasured several times, it was transposed onto two axes, as shown in Fig. 10. The 1st principal axis was set to the direction in the largest dispersion of datum and 2nd principal axis to the direction in the second largest dispersion of datum in a multicomponent analysis. This demonstrates the ability to cluster points roughly in types according to their species and quantity. However, it was difficult to clearly classify the 6000 ppm propane and 2000 ppm butane as they are located close to each other. Therefore, to precisely classify clusters with similar characteristics and overcome statistical variances, a gas pattern recognizer using a multi-layer neural network was employed along with an error back propagation learning algorithm, which is known to be effective in classifying and identifying complex nonlinear patterns [22].

3.3. Implementation of gas pattern recognizer and gas recognition system

Using the sensitivity signals from the sensor array as multi-dimensional input patterns, a gas pattern recognizer using a multi-layer neural network with an error back propagation learning algorithm was then implemented [22–24]. The neural network consisted of an input layer with nine nodes which received the data from the sensors on the sensor array, a hidden layer with eight neurons, and an output layer with nine nodes as shown in Fig. 11. The nine nodes in the output layer indicated the recognition results for three concentration levels of three kinds of explosive gases, butane, propane, and methane. Fig. 11 shows the recognition result in the case of an injection of 2000 ppm propane gas. In this study, the experimental data were measured in triplicate with 2000, 4000, and 6000 ppm concentrations of methane, propane, and butane. The learning process was repeated until the learning error reached 0.0001.

The implemented gas recognition system is shown in Fig. 12. An analog multiplexer, filter, and signal transformer for level shifting were all included in a data acquisition board for transferring the multi-signal to a digital signal processor (DSP) board. The learned connection-weights were then saved in the DSP board memory. For real time processing, the recognized gas species and concentrations can then be displayed on a liquid crystal display (LCD).
A photograph of the fabricated explosive gas-recognition system using a DSP board is shown in Fig. 13. The specific recognition results for the proposed explosive gas recognition system with 2000 ppm butane, 4000 ppm propane, and 6000 ppm methane are shown in Fig. 14. After learning, the proposed gas recognition system demonstrated an almost 100% recognition rate. To verify this recognition rate, new data was generated with a 5% error in the original data and the resulting recognition rate was examined. It also showed a high recognition rate of about 99%.

![Figure 11. Multi-layer neural network for gas recognition system.](image1)

![Figure 12. Architecture of proposed gas recognition system for identification of explosive gases.](image2)

![Figure 13. Picture of implemented explosive gas recognition system.](image3)
4. Conclusion

To recognize the species and quantity of explosive gases under a low explosion limit, the sensor array with nine SnO₂/Ca,Pt-based metal oxide sensors integrated in an alumina substrate were fabricated. The SnO₂/Ca,Pt base material was prepared using coprecipitation, and it exhibited a particle size of about 7 nm, a high specific surface area of 35 m²/g, a rutile structure after being calcined at 600°C for 1 h, and long-term stability. To give good selectivity to the sensors, several additives including Pt, Pd, Au, CuO, La₂O₃, Sc₂O₃, TiO₂, WO₃, and ZnO were mixed with the base material. The resulting sensor arrays showed high and selective sensitivities and long-term stability to low gas concentrations at 400°C.

Using the sensing signals from the sensor array along with a multi-layer neural network using an error back propagation learning algorithm, an intelligent gas recognition system with a DSP board was implemented in order to produce a real time recognition system for explosive gases such as butane, propane, and methane. Furthermore, the fabricated gas recognition system could precisely classify and identify the species and concentration of each gas in real time processing.

In future, the implementation of a sensor array and system that can recognize continuously varying concentrations and specific gases in a mixture of gases will be attempted. Finally, a real time small-sized system that can consider environmental conditions like peripheral temperature and relative humidity will be designed to detect possible leakages of explosive gases and recognize the species and quantity of specific gases in gas pipes or workplaces.

References


