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A Planar Gas Sensor Combined with Interdigitated Array Electrodes

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Keywords Interdigitated array electrodes, redox cycles, hydrogen gas sensor

Interdigitated array (IDA) electrodes are used for the determination of components contained in aqueous solutions with high sensitivity.1-7 Redox cycles are generated between the two working electrodes; they are called the generator and the collector, and are placed close to each other. The generator current increases when a suitable potential is applied to the collector (a dual-mode), compared to a single-mode when the collector is electrically open. In a previous study8, IDA electrodes were applied to gas detection for the first time. The electrodes were fabricated on a gas-permeable membrane in order to obtain good response to the gases (NOx) through improved conventional photolithography. It was confirmed that the IDA electrodes are useful in a gas-detection system, as well as in solution systems. Generally, the gap and width of the electrodes should be small in order to generate a large number of redox cycles. However, it was difficult to fabricate fine patterns on the gas-permeable membrane, because the membrane was flexible and its surface was not flat. On the other hand, it is already possible to fabricate fine IDA patterns on a hard and flat substrate and are already being marketed. However, if these electrodes fabricated on substrate are set in an electrolyte solution, they do not come into contact with the membrane. Therefore, it is said that the sensitivity and response speed are poor. Accordingly, we experimented with a new method of applying IDA electrodes to a gas-sensing system. We call it a planar IDA gas sensor. A piece of filter paper containing an electrolyte solution was put on IDA electrodes, which were fabricated on a glass substrate. This gas sensor was very easy to construct. A similar planar sensor had been reported for amperometric sensing of oxygen.9 It was developed as a low-cost and disposable sensor, and applied to glucose sensing. A planar sensor is expected to be more useful in complicated detection systems i.e., using IDA electrodes, which was confirmed after being used in a hydrogen-detection system.

Experimental

Propylene carbonate (PC) was purchased from Nacalai Tesque Inc. Tetraethylammonium perchlorate (TEAP) was prepared from tetraethylammonium bromide and perchloric acid, both of which were obtained from Wako Chemical Co. The precipitate of TEAP was purified by recrystallization from water and stored in an evacuated desiccator after baking at 100°C. A PC solution containing 0.1 M TEAP was prepared as an electrolyte.

A planar IDA gas sensor was prepared based on available IDA electrodes (No. 2047 from BAS). The width and gap of the electrodes were 10 μm and 5 μm, respectively. The valid length of the electrode was 2 mm, and the number of electrodes was 65 pairs. The area of each electrode was 1.3 mm². The IDA and the

Fig. 1 Structures of planar gas sensors combined with IDA electrodes. The IDA electrodes used were fabricated on a glass substrate. The bandwidth of the generator and the collector were 10 μm, and the gap between them was 5 μm. These electrodes were made of Au. A piece of filter paper (No. 5C, 6 mm×6 mm) was placed on the electrodes, and 20 μl of electrolyte was dropped onto the paper.
counter electrodes were made of Au. A reference electrode was simply prepared as follows. A 10-mM AgNO₃ aqueous solution was dropped onto the electrode after electrical plating with Ag; it was then dried at room temperature. A piece of filter paper (6 mm × 6 mm, No.5C) was put on the electrodes and 20 μl of the electrolyte was dropped onto the paper using a 10-μl micro-syringe. A schematic of the sensor is shown in Fig. 1.

The planar IDA gas sensor was placed in a vinyl bag (100 mm × 140 mm) which had a zipper. Hydrogen mixed in nitrogen, in arbitrary concentrations, was allowed to flow into the vinyl bag at a flow rate of 100 ml min⁻¹, and was overflowed through a small opening in the zipper. The gas was controlled with the help of mass-flow controllers and stop valves. Cyclic voltammograms were measured using a dual-potentiostat, which was previously described.⁸

Results and Discussion

In the first study of gas sensing using IDA electrodes⁸, the reaction system on the electrodes was complicated, because there were many reactions concerned with redox of the analytes (NOₓ) and their products, and their standard potentials were similar to one another. In contrast, in this study, the hydrogen-sensing properties of the IDA electrodes were examined, and it was expected that simple redox cycles (Eq. (1)) were generated between the generator and the collector in an inert environment.

\[
2H^+ + 2e^- \rightleftharpoons H_2 \quad E^o: 0.000 \text{ V} \tag{1}
\]

In this study, a non-aqueous solution and nitrogen were used as the electrolyte and the carrier gas in order to prevent the reaction of hydrogen with hydroxide ion (Eq. (2)) and the reaction of protons with oxygen (Eq. (3)), respectively.

\[
2H_2O + 2e^- \rightleftharpoons H_2 + 2OH^- \quad E^o: -0.8281 \text{ V} \tag{2}
\]

\[
O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O \quad E^o: +1.229 \text{ V} \tag{3}
\]

Before evaluating the planar IDA gas sensor, we examined the IDA electrodes that were fabricated on a gas-permeable membrane and were constructed in the same manner as before.⁸ Two kinds of electrodes, i.e., made of Au and Pt, were examined. The measurements were carried out using potentiostatic electrolysis. The results are shown in Fig. 2. When the Pt electrodes were used, the response of the working electrode was about 10-times greater than that in the case of the Au working electrode. In the dual-mode, however, a reasonable negative response was not obtained, even when the collector potential was shifted down to −2.0 V vs. Ag/Ag⁺. In this way, the material that was active to the analyte was not proper for the generation of redox cycling. On the other hand, negative responses of the collector current were observed in the case of Au, and the responses of the Au generator became larger than those obtained in the single-mode. The collection efficiency and the amplification rate were estimated from these calibration curves to be 0.42 and 1.52, respectively.

In this experiment mentioned above, the dimensions of the IDA electrodes were 100 μm both in width and in gap, the same as reported in a previous paper.⁸ The amplification rate could be improved dramatically by miniaturizing the IDA electrodes. However, it is difficult to fabricate fine electrode patterns on a flexible and uneven membrane; at least this is the present situation. Consequently, another approach was examined. Instead of fabricating IDA electrodes on a membrane, the gas sensor was constructed based on finely patterned IDA electrodes fabricated on a glass substrate. Electrodes made of Au were chosen because they were confirmed to generate redox cycles in a preliminary investigation. Filter paper was placed on the electrodes, and the electrolyte was dropped on to the filter paper. The electrolyte spread uniformly and was contained as a thin layer within the filter paper. This
Fig. 3 Voltammograms of the planar sensor in the presence of hydrogen. Curves (a), (b) and (c) are cyclic voltammograms of the generator in the single-mode, and the generator and collector in the dual-mode, respectively. They were obtained in 1000-ppm H₂/N₂. The sweep rate was 50 mV/s, and the collector potential was held at -0.5 V in the dual-mode.

allowed the electrodes to be only slightly separated from the gas phase. Consequently, a good response was expected, just as with the electrodes on a gas-permeable membrane. For evaluating the sensor, cyclic voltammetry (not potentiostatic electrolysis) was used because of the poor durability of the electrodes. Figure 3 shows the cyclic voltammograms obtained in 1000 ppm of hydrogen. In the single mode (a), the current of the electrode increased along with a rise in the potential. When hydrogen was absent, no increase in the current was observed. Curves (b) and (c) correspond to the cyclic voltammograms of the generator and collector currents in the dual-mode. The collector current was also increased and the generator current was about 3.5-times greater than the single-mode current. This amplification rate is much greater than that obtained using the membrane electrodes. In this way, this type of the sensor had good characteristics despite its simplicity.

The vapor pressure of the solvent PC is low enough to use the sensor for a few hours. For example, the vapor pressure is 1.255 mmHg at 25°C, about 1/20th of the water vapor pressure. However, unfortunately, the lifetime of the electrodes was not long. The electrodes could not work after only a few times of applying the potential sweep, confirmed by an optical-microscopic observation. The damaged metal films of the electrodes exfoliated from the substrate, and the generator and the collector short-circuited each other. Although finely patterned electrodes have a tendency to become easily damaged, the planar IDA gas sensor has the ability of wide use, if, in the future, the problem of film exfoliation is solved by tightly depositing the film onto a substrate.

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References


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