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Selective detection of acetylene gas extracted from isolation oil by an electrochemical sensor using a gold electrode

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The selective detection of acetylene in gases extracted from isolation oils has been studied to develop an electrochemical sensor for the diagnostic monitoring of the condition of in-service electrical instruments. Effects of coexisting gases (CH_4, C_2H_6, C_2H_4, H_2 and CO) on the oxidation current of C_2H_2 were tested using gas-permeable gold-coated and platinum-black electrodes as the sensor. The gold-coated electrode showed good behaviour for the selective current detection of acetylene under potentiostatic conditions (– 0.1 V/Pt-black reference electrode) in 10 M H_2SO_4 electrolyte solution.

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1. Introduction

The analysis of gases evolved in isolation oil is generally used to diagnose the working condition of power transformers and electric cables, since the gases, such as hydrogen, carbon monoxide and some hydrocarbons, are generated upon the decomposition of the isolation oil [1–3]. The analysis of the gas extracted from the isolation oil provides useful information about the type of faults in the electric instruments, because the kinds of gases and the rate of gas generation can be related to the type and severity of the fault. In particular, acetylene is generated by an arcing discharge in a transformer, so that the detection of acetylene is important to set limits for the safe use of the transformer.

In ordinary gas analysis, the gas components are extracted from the isolation oil in an electric instrument and determined by gas chromatography. A simpler detection method for these gases, in particular for acetylene, would be useful for the analysis of gases and for a preliminary diagnosis of the condition of the electrical instruments.

Recently, simple gas sensors have become widely used for the monitoring of gases in a variety of applications. Gas sensors, such as thermal conductivity detectors with catalytic material, and semiconductor sensors [4–6], are useful for detection of combustible gases. However, they are unusable for the selective detection of acetylene because of the significant interference due to hydrogen and methane. Some electrochemical sensors using platinum black electrodes have also been reported for the detection of carbon monoxide [7–10], hydrogen and hydrocarbons. They do not, however, have high selectivity for acetylene in air containing gases such as the extracted gas from isolation oils.

In this study, we have investigated the electroanalytical properties of an amperometric gas sensor with either a gas permeable platinum black or a gold electrode. The gold electrode showed high selectivity for acetylene in mixed gases containing hydrogen, carbon monoxide, ethylene and some aliphatic hydrocarbons. It was found that the electrochemical sensor using a gas permeable gold electrode combined with a gas extractor can be used for the detection of acetylene for diagnostic monitoring of the life of electric instruments. Additionally, the sensor, combined with a simple column gas separator, showed desirable properties for detailed diagnosis of the working condition of transformers.

2. Experimental details

A schematic diagram of the gas sensing system used is shown in Fig. 1. The sensor is constructed as a three electrode cell system containing 2 cm^3 of a 10 M H_2SO_4 aqueous solution. Gas permeable electrodes were used as working electrodes (WE). A platinum black film having about 200 μm thickness was printed on to a porous polytetrafluoroethylene (PTFE) membrane (Sumitomo Electric Ind., Ltd, FT-30) and the gold thin film ($\sim 0.3\ \mu$m) was vacuum deposited on PTFE to make the gas permeable working electrode. The diameter of the WE was 1.8 cm. Plantinum black electrodes were used as reference (RE) and counter electrodes (CE). These electrodes were made by printing the electrode on the cell wall. The potential of the RE was 0.8 V against an Ag/AgCl–sat.KCl electrode.

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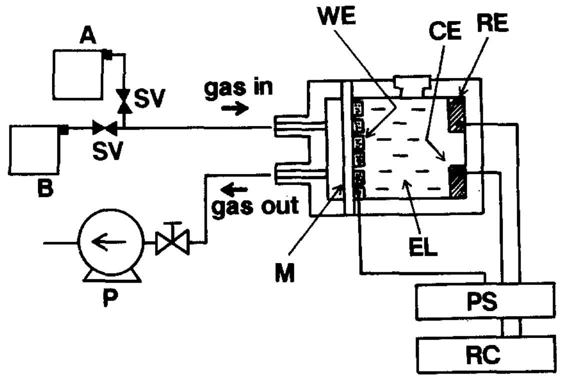

Fig. 1. Schematic diagram of the electrochemical sensor and gas sensing system. (A) pure air reservoir, (B) sample gas reservoir, (SV) stop valve, (P) suction pump, (M) gas permeable membrane, (EL) electrolyte, (PS) potentiostat, (RC) recorder.

Sample gases were prepared by a mixing method in which a known volume of the reaction gas was added to pure air (< 0.1 p.p.m. impurity). The sample gases were stored in gas sampling bags and sucked to the sensor by a pump. The gas flow rate into the sensor was 200 cm^3 min^{-1}.

The current–potential characteristics of the sensors were measured by a potentiostatic method at each electrode potential. The potential was held about 30 min to stabilize the residual current obtained with a pure air flow. The current response for the reactive gases was recorded on a chart recorder, as shown in Fig. 2. The steady state currents were observed about 20 s after beginning of the sample gas flow. All measurements were carried out at 20 ± 2 °C.

A flow injection method was also used, and is described in the text.

3. Results and discussion

3.1. *PtBE sensor*

A sensor with a platinum black printed electrode (PtBE) was employed to measure the current response for various gases which are components of the extracted gas from isolation oils.

Anodic currents for the oxidation of acetylene, ethylene, hydrogen and carbon monoxide were measured as a function of time at an electrode potential of 0.1 V, as shown in Fig. 2. The volume concentrations of the reactive gases in the sample gases were 20, 50, 300 and 200 p.p.m. for C_2H_2, C_2H_4, H_2 and CO, respectively, which are similar to the concentrations of the gases from isolation oil [11].

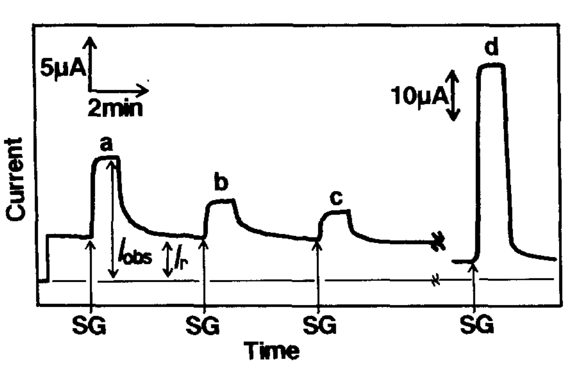

Fig. 2. Current response curves obtained by PtBE sensor for the reactive gases. Electrode potential, 0.1 V/RE in sensor. Gas flow rate, 200 cm^3 min^{-1}. SG, starting point of sample gas flow. (a) 20 p.p.m. C_2H_2, (b) 50 p.p.m. C_2H_4, (c) 300 p.p.m. H_2, (d) 200 p.p.m. CO.

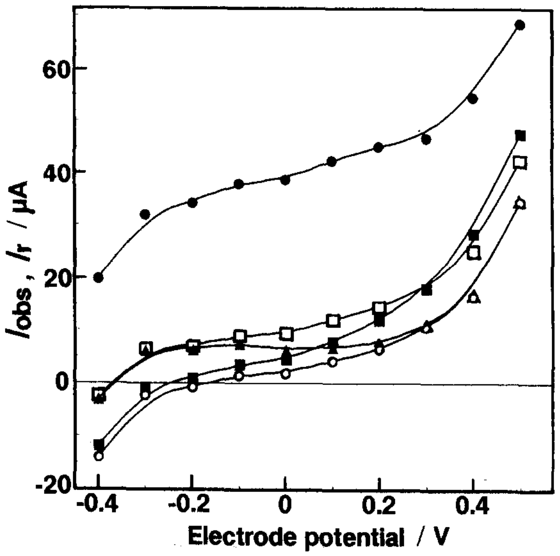

Fig. 3. Potential dependence of steady state current, I_{obs}, and residual current, I_r, obtained by PtBE sensor for various gases; (●) 200 p.p.m. CO, (▲) 300 p.p.m. H_2, (■) 50 p.p.m. C_2H_4, (□) 20 p.p.m. C_2H_2 and (○) pure air.

The steady state oxidation currents, I_{obs}, were plotted as a function of the electrode potential, E, as shown in Fig. 3. The open circles in the figure show the residual current, I_r, obtained for the pure air. $|I_r|$ increases at near − 0.4 V and 0.4 V, which is attributed to the reduction of oxygen (and/or platinum oxide) and oxidation of platinum, respectively. The current response was observed for alkane gases at almost the detection limit, CH_4 and C_2H_6, in this potential region, so that the data were not plotted in the figure.

From these results, the real oxidation current for the gases, $I_{ox} = I_{obs} - I_r$, and the current sensitivity, $J_{ox} = I_{ox}/C_G$, can be calculated where C_G is the

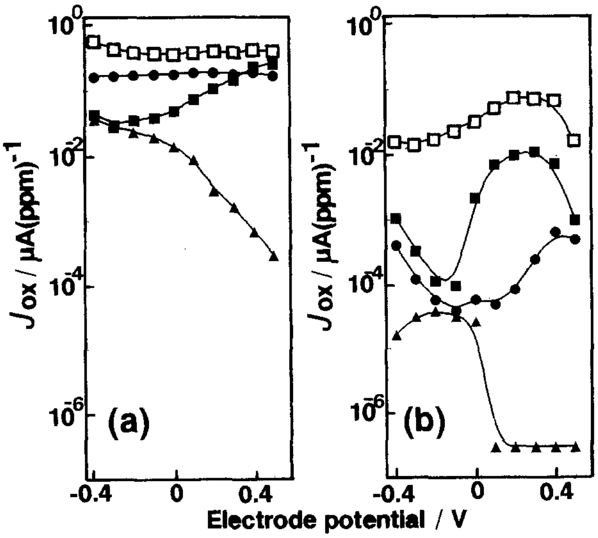

Fig. 4. Potential dependence of the current sensitivity obtained by PtBE sensor (a) and AuCE sensor (b) for various gases, (●) CO, (▲) H_2, (■) C_2H_4 and (□) C_2H_2.

volume concentration of the reactive gas in the sample gases in p.p.m. Fig. 4(a) shows the $J_{ox} - E$ relationship, which indicates that the current sensitivities are different with each gas. $J_{ox}(C_2H_2)$ is the highest for these gases. $J_{ox}(C_2H_2)$ and $J_{ox}(CO)$ do not depend on the electrode potential, however, $J_{ox}(C_2H_4)$ and $J_{ox}(H_2)$ are dependent on the electrode potential.

3.2. *AuCE sensor*

The anodic current of the sensor using the gold coated electrode (AuCE) was measured to compare with the PtBE sensor. The steady state oxidation current, I_{obs}, was plotted against the electrode potential, as shown in Fig. 5. A low residual current was obtained in the potential domain ranging from -0.4 V to 0.1 V. $I_{ox}(CH_4)$ and $I_{ox}(C_2H_6)$ were also much smaller than those of $I_{ox}(C_2H_2)$.

The current sensitivities for gases, J_{ox}, depend on the electrode potential, Fig. 4(b). The $J_{ox}(C_2H_2)$ of the AuCE sensor is about one-tenth of that of the PtBE sensor. This observation can be explained from the ratio of surface areas of AuCE and PtBE, which were estimated from the ratio of the reaction currents for $[Fe(CN)_6]^{3-}$ reduction at the electrodes. In contrast, $J_{ox}(CO)$ and $J_{ox}(H_2)$ for AuCE are less than 0.2% of those for PtBE at $E = 0.1$ V. Such a remarkable difference between the electrodes may be caused by a difference in the catalytic nature of the electrodes.

$J_{ox}(C_2H_2)$ is independent, but J_{ox} of CO, C_2H_4 and H_2 depend on the electrode potential. The optimum conditions for selective detection of C_2H_2 should be considered.

3.3. *Selectivity of acetylene*

The selectivity for acetylene against the other gases defined as $S(C_2H_2/\text{G}) \equiv J_{ox}(C_2H_2)/J_{ox}(\text{G})$ was plotted against the electrode potential in Fig. 6, where G indicates the coexisting reactive gas, H_2, CO or C_2H_4.

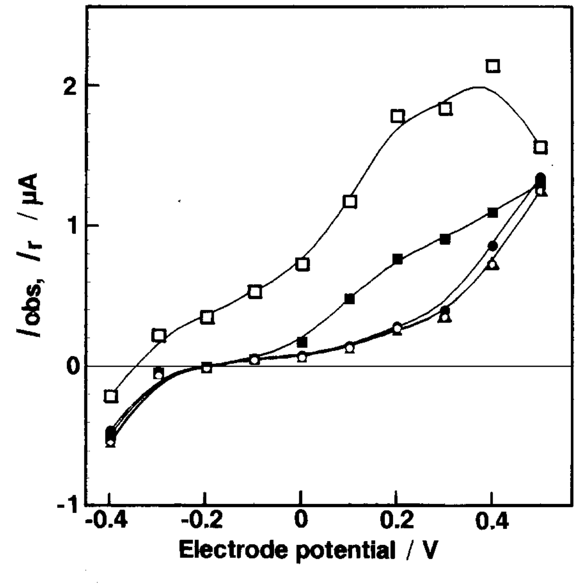

Fig. 5. Potential dependence of steady state current, I_{obs}, and residual current, I_r, obtained by AuCE sensor for various gases: (●) 200 p.p.m. CO, (▲) 300 p.p.m. H_2, (■) 50 p.p.m. C_2H_4, (□) 20 p.p.m. C_2H_2 and (○) pure air.

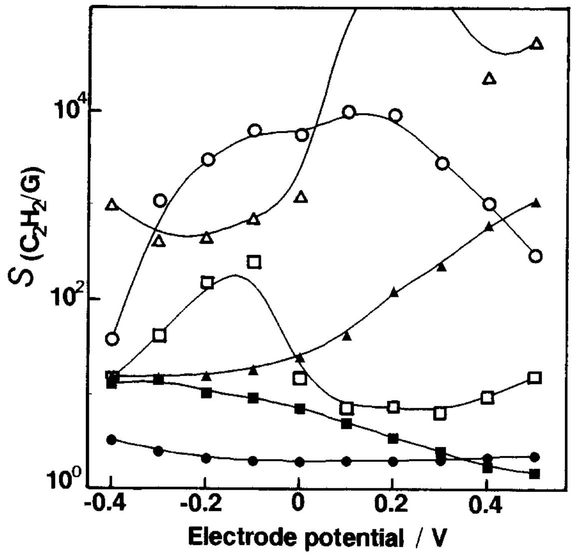

Fig. 6. Potential dependence of acetylene selectivity against the gases of CO (●, ○), H_2 (▲, △), C_2H_4 (■, □) obtained by PtBE sensor (●, ▲, ■) and by AuCE sensor (○, △, □).

In the case of PtBE, $S(C_2H_2/CO)$ is less than 5 in the whole potential region and $S(C_2H_2/C_2H_4)$ is also less than 5 in the positive potential region. On the other hand, AuCE shows high selectivity for acetylene; in particular, the $S(C_2H_2/\text{G})$'s are higher than 100 at $E \simeq -0.1$ V. These results suggest that the selective detection of acetylene can be performed by AuCE with the optimum electrode potential in this region.

3.4. *Flow injection method*

The acetylene concentration – current linearity and the selectivity of acetylene with a flow injection method have been tested as a practical method of gas detection. The schematic diagram of the flow injection method using the AuCE sensor, a gas sampler and a gas extractor is shown in Fig. 7. A constant volume ($5\,cm^3$) of sample gas is taken by the gas sampler, which is carried into the sensor by a carrier gas (pure air).

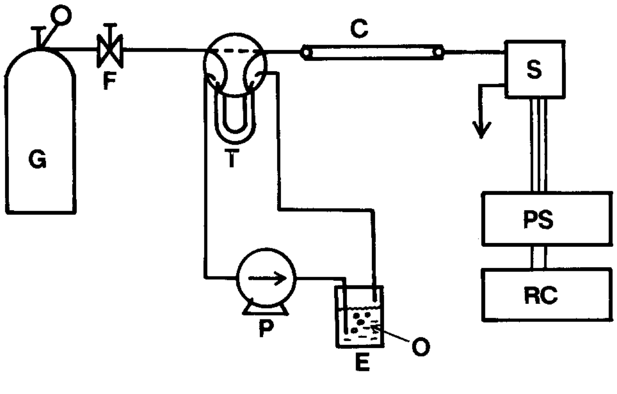

Fig. 7. Schematic diagram of flow injection method for the detection of gases extracted from isolation oil. (G) carrier gas, (F) flow control valve, (T) gas sampler ($5\,cm^3$), (P) suction pump, (E) extractor, (O) isolation oil, (C) connection tube, (S) AuCE sensor, (PS) potentiostat, (RC) recorder.

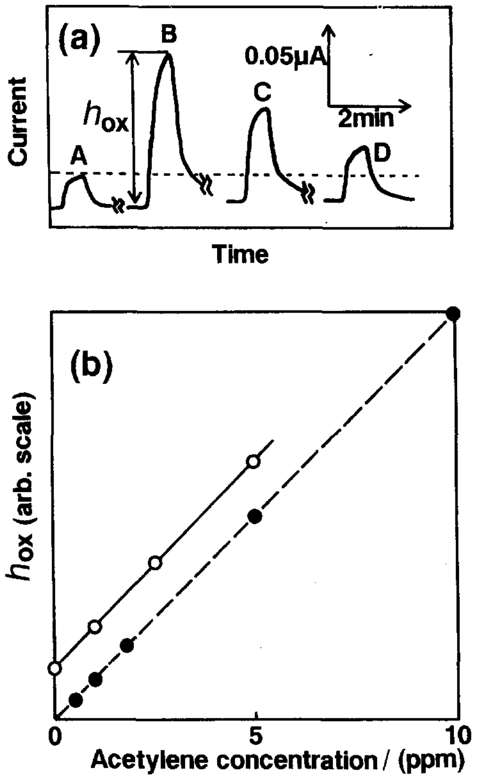

Fig. 8. Current–time response (a) and current–acetylene concentration relationship (b) obtained by the flow injection method. In Fig. 8(a), the gas containing 200 p.p.m. CO, 300 p.p.m. H_2 and 100 p.p.m. C_2H_4 with C_2H_2 of 0 p.p.m. (A), 5 p.p.m. (B), 2.5 p.p.m. (C) and 1 p.p.m. (D). In Fig. 8(b), (- - -) the sample gas containing C_2H_2 without other reactive gases, (——) gas component is the same as indicated in Fig. 8(a).

The typical current–time responses for sample gases observed are shown in Fig. 8(a). The wave height, h_{ox}, is plotted against the acetylene concentration, C_A, in the sample gases. The broken line in Fig. 8(b) shows a linear relationship between h_{ox} and C_A for the sample gas containing acetylene without other reactive gases. The error observed was within 0.2 p.p.m. of the C_2H_2 concentration. For practical use, 10 p.p.m. acetylene gas was used for calibration of the h_{ox}–C_A relation of each sensor, because the sensors have slightly different sensitivities depending on their effective electrode surface areas.

To elucidate the effect of coexisting gases on the current, the current response for sample gases containing 200 p.p.m. H_2, 300 p.p.m. CO, 100 p.p.m. C_2H_4 and various concentrations of C_2H_2 were measured (see Fig. 8(a)), and h_{ox} is plotted against C_A in Fig. 8(b). A linear relationship is obtained; however, the effect of coexisting gases on h_{ox} is not negligible in the case of low C_A. Under such detection conditions, about 1 p.p.m. acetylene is the detection limit for the monitoring of the condition of electrical instruments. For example, the dotted line in Fig. 8(a) indicates the limiting level for the acetylene concentration of 1.2 p.p.m. in the sample gases. This relationship suggests that the AuCE sensor could be useful for diagnostic monitoring of the conditions of electric instruments.

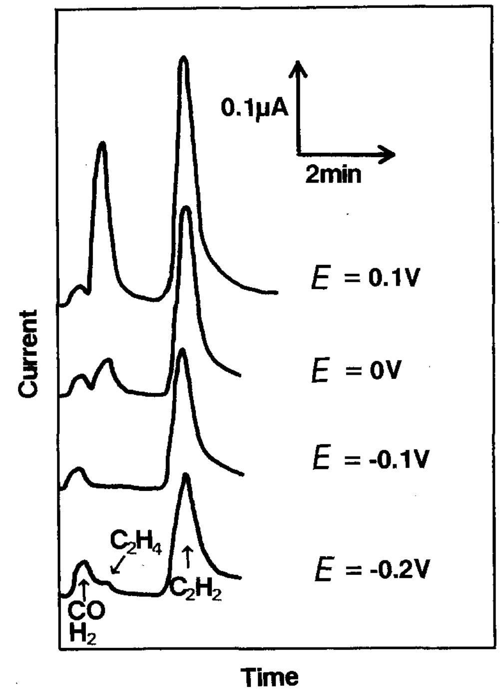

Fig. 9. Current–time responses obtained by AuCE sensor with the simple column (50 cm long of activated aluminium column) at various electrode potential. 5 cm^3 of sample gas containing 318 p.p.m. H_2, 226 p.p.m. CO, 88 p.p.m. CH_4, 30 p.p.m. C_2H_6, 49 p.p.m. C_2H_4 and 12 p.p.m. C_2H_2.

For a detailed analysis of acetylene in the sample gases, a simple gas chromatography column should be connected instead of the connection tube as shown in Fig. 7. Current peaks for C_2H_4, CO and H_2 are clearly separated from the acetylene peak on a current–time chart, as shown in Fig. 9. The current sensitivities of the gases depend on the electrode potential. C_2H_4 is separately detectable at $E = 0.1$ V, and the interference by C_2H_4 on C_2H_2 is effectively eliminated at $E = -0.1$ V. A simple separation column – AuCE sensor system has been shown to allow for the diagnostic analysis of gases extracted from the electric instrument.

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