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Detection and Quantification of CO Gas Based on the Dynamic Response of a Ceramic Sensor

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A novel method of gas-sensing is proposed based on the information of nonlinear, dynamic response of a ceramic gas sensor. A sinusoidal voltage is applied to a heater equipped with a SnO_2 gas sensor and the resulting output resistance is analyzed by the Fast Fourier Transformation (FFT). It was found that the intensities of the higher harmonics exhibit characteristic changes with respect to different kind of gas.

Recently, we have developed a novel sensing method for quantitative characterization of electrochemical nonlinearity by analysis of the higher harmonics obtained from FFT on the output current.[1,2] As an extension of this study, we have measured the dynamic response of a ceramic sensor with the application of sinusoidal voltage.

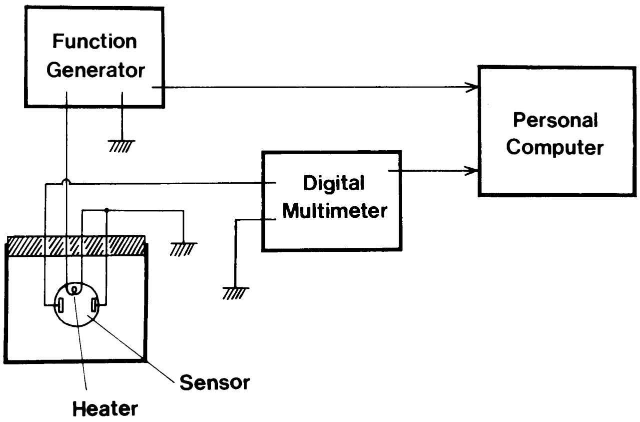

Fig. 1. Experimental apparatus.

Figure 1 shows the experimental apparatus. A sinusoidal voltage (f:0.02/Hz, $1.5+1.5\cos 2\pi ft$/V) is applied to the heater of a gas sensor. The a.c. voltage waveform and the electrical resistance of the gas sensor were successively stored in a NEC PC-9801 personal computer, and then Fourier-Transformed to the frequency domain. A SnO_2 gas sensor, TGS813 (commercially available from Figaro Engineering Inc., Osaka),[3-5] was used. The electrical resistance was measured with a digital multimeter (Yokogawa, Model 7552, Japan). The volume of the glass-cell was 100 ml. Major part of the glass-cell was immersed into a water bath (25.0±0.5 °C). Desired amount of gas was introduced into the glass-cell with a glass injector. All measurements have been carried out after the application of sinusoidal voltage with more than ten cycles. After 10 cycles, the resistance vs. voltage (R vs. V) curve showed an almost closed cycle, indicating that the experimental system became a quasi-steady state. Under these conditions, the temperature of the ceramic surface changed within the range of 100 and 300 °C.

Figure 2 shows the R vs. V curve, for different kind of gas. The R vs. V curves for different gases are apparently different each other. The characteristic response for each gas is attributable to the difference 1) in the temperature dependence of the conductance of the sensor in the presence of the adsorbed gas, 2) in the kinetics of adsorption or desorption of gas on the ceramic surface, and 3) in the kinetics of the oxidative reaction of gas on the surface. We have carried out at least four independent measurements for a fixed experimental condition. It was confirmed that the estimated experimental error was less than 5 % throughout the measurement. With the repeated application of relatively

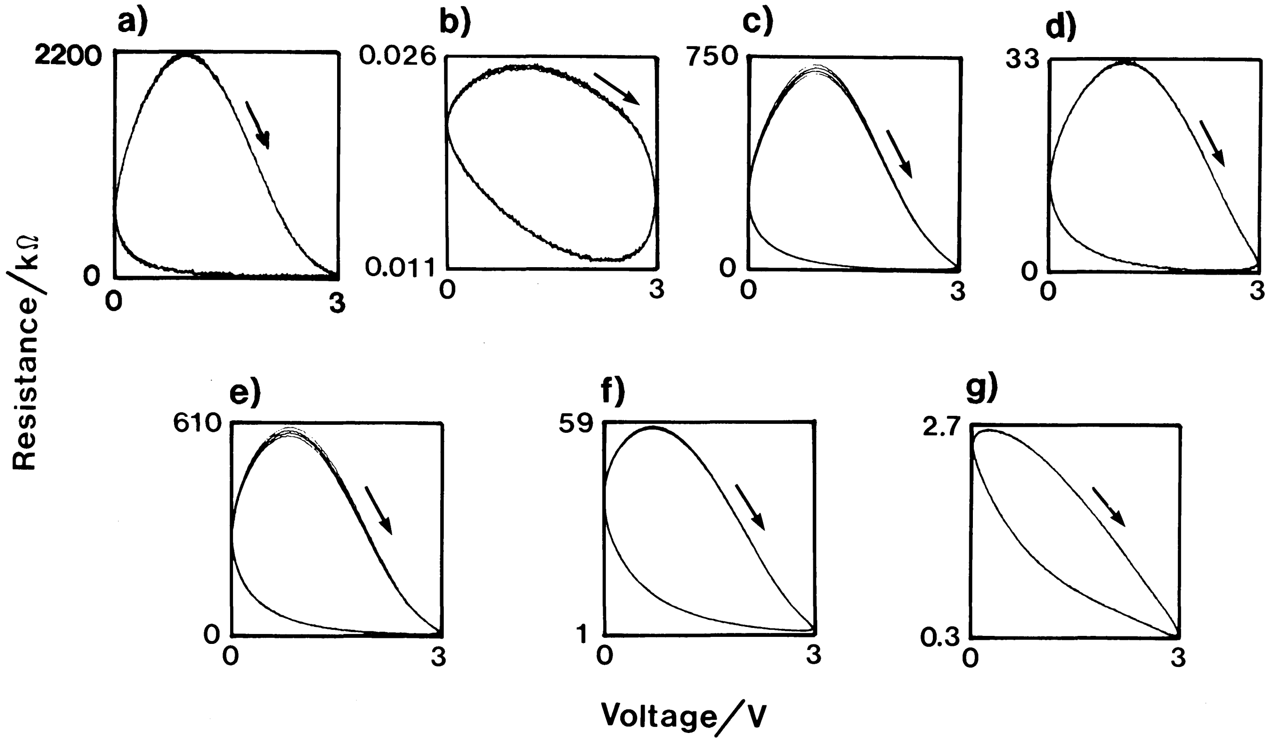

Fig. 2. Characteristic response of resistance-voltage curve for a) clean air as a control, b) hydrogen sulfide, c) ethanol, d) ammonia, and e)-g) carbon oxide gas. The concentration of the gas was 4.0 mol·m^{-3} in b), c), d), g), 0.4 mol·m^{-3} in e), and 0.8 mol·m^{-3} in f).

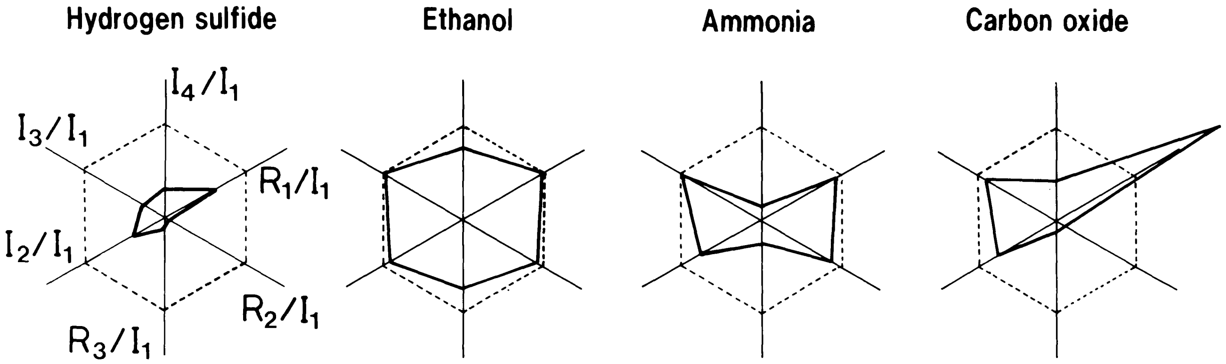

Fig. 3. Characteristic responses of the relative intensities of the higher harmonics. R_i and I_i are the real and imaginary components of the i_{th} higher harmonics.

high voltage (3 V in this study), the adsorbed chemical species may be completely eliminated from the ceramic surface. This process corresponds to the repeated cleaning of the sensor and, thus, affords us high reproducibility on the shape of the resistance-voltage curve. In order to analyze the characteristics of the time dependence of the resistance in a quantitative manner, time tracing of the resistance was Fourier transformed to the frequency domain. Then, the intensities of the 2nd, 3rd, and 4th harmonics were normalized relative to that of the imaginary component of the first harmonics I_1 (Fig.3). It is apparent that one can distinguish various gases by measuring the changes of the relative intensities.

Figure 4 shows the relative intensities of the higher of harmonics vs. the concentration of carbon oxide. This suggests that the concentration of carbon oxide can be obtained based on the changes of the higher harmonics.

Let us briefly discuss on the source of the "higher harmonics" appeared in the output signal. If one considers the kinetics of adsorption and desorption of a gas species on the surface of the ceramic body, the following equation may be derived.

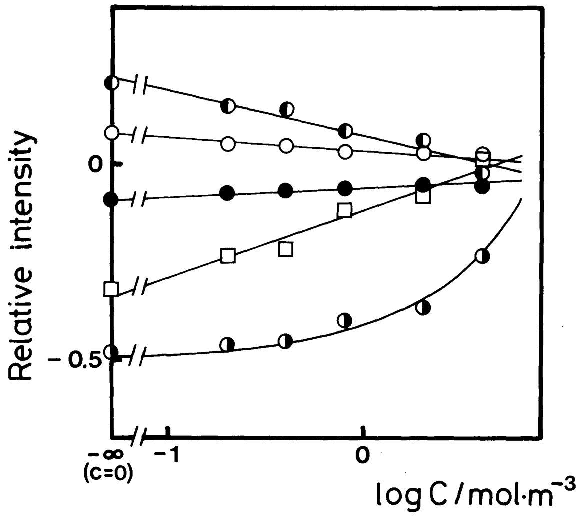

Fig. 4. Dependence of relative intensities on the concentration of carbon oxide.
□: R_2/I_1, ◐: R_3/I_1, ◑: I_2/I_1, ●: I_3/I_1, and ○: I_4/I_1.

$$\frac{d\Gamma}{dt}=k_1x(\Gamma_0-\Gamma)-A\Gamma\exp\left(\frac{-E_a}{RT}\right) \qquad (1)$$

Where, x: concentration of gas in the bulk phase, Γ: concentration of the adsorbed gas, Γ_0: saturated concentration of the adsorbed gas, k_1: rate constant of adsorption, A: a constant (frequency factor), E_a: activation energy of desorption, R: gas constant, and T: absolute temperature. When the temperature is changed in a sinusoidal manner, as $T=T_0+T_1\cos\omega t$, Eq.1 is expanded as Eq.2 under the condition of $T_0>>T_1$.

$$\frac{d\Gamma}{dt}=k_1x(\Gamma_0-\Gamma)-A\Gamma\exp\left(\frac{-E_a}{RT}\right)\left\{1+\frac{E_a}{RT_0{}^2}\Delta T+\left(-\frac{E_a}{RT_0{}^3}+\frac{E_a{}^2}{2R_2T_0{}^4}\right)\Delta T^2+\cdots\right\} \qquad (2)$$

where $\Delta T=T_1\cos\omega t$. When one notices that $\Delta T^2=T_1{}^2(1+\cos2\omega t)/2$, it is clear that Eq.2 contains the higher harmonics. Using the mathematical analysis of the harmonic balance method,[6)] one can evaluate the higher harmonic components from the kinetics of adsorption and desorption. In addition to the above effect, temperature dependences of k_1, Γ_0, and also the gas-pressure may contribute to the higher harmonics, as well as the effect temperature dependence of the conductance and the rate of heat transfer around the ceramic body. Detailed discussion on the theoretical treatment including these effects will be given in a separate manuscript.

Currently, gas sensing by ceramic material has been carried out based on the information of the change of the resistance. However, if one wishes to distinguish various kind of odour molecules, solely the change of resistance is insufficient. At the present time, our results are only preliminary. However, it is apparent that the present method affords us abundant information based on the relative intensities of the higher harmonics.

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