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Discrimination of Drinks with a Novel Sensing System Detecting Electrochemical Nonlinearity

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We propose a novel strategy for the development of a chemical sensor based on the information of electrochemical nonlinearity. A sinusoidal voltage is applied to a test solution and the resulting output current is analyzed by the Fast Fourier transformation (FFT). From the higher harmonic components in the FFT, voltage dependences of both capacitance and conductance are evaluated. This method may become a powerful analytical tool with the selection of suitable metal electrodes.

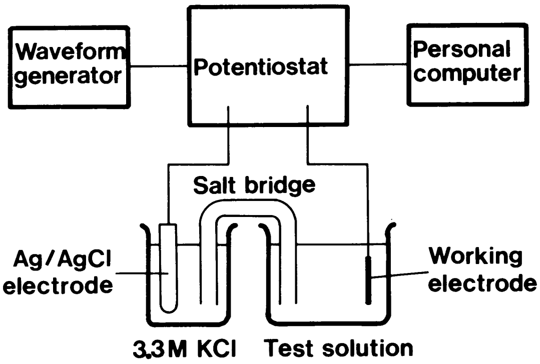

Fig. 1. Experimental apparatus.

In general, the electrochemical characteristics of a solid/liquid interface are highly nonlinear, i.e., the capacitance and conductance change markedly depending on the applied voltage. Recently, we have developed a novel sensing method for quantitative characterization of the electrochemical nonlinearity by analysis of the higher harmonics obtained from FFT of the output current.1) As an extension of this study, we have measured the nonlinear characteristics of various commercial drinks by using platinum, carbon, silver, and gold electrodes. It was found that the nonlinearity changes markedly, depending on the metal used as the electrode.

Figure 1 shows the experimental apparatus. A sinusoidal voltage (1 Hz, 1 V) is applied to the test solution and the time trace of the output current is analyzed by FFT. Details of the experimental method have been described in a previous study.1) Under these conditions, the capacitive component at the electrode is dominant, compared with that due to the dielectricity of the bulk solution.2) Each test solution of the commercial drinks was measured at 20±1 °C without any pretreatment. Sample A was can coffee (Ueshima Coffee Co. Ltd., Hyogo) and was composed of coffee extract, skim milk, whole milk, sugar, and grape sugar. Sample B was black tea (Kirin Brewery Co. Ltd., Tokyo) and was composed of tea, sugar, vitamin C, and perfume. Sample C was "alkali ion" drink (Otsuka Pharmaceutical Co., Ltd., Tokyo) containing sugar, grape sugar, fructose, citric acid, sodium citrate, sodium chloride, vitamin C, potassium chloride, calcium lactate, L-glutamic acid sodium salt, magnesium chloride, and perfume. Sample D was the drink of lactic acid bacteria (Yakuruto Co., Ltd., Osaka) and was composed of sugar, grape sugar, fructose, skim milk, perfume, and lactic acid bacteria. The working electrodes used for the measurement were platinum, gold, and silver wires of 20 mm length and 0.5 mmϕ, and a carbon rod of length 20 mm and 3.0 mmϕ. All of the materials used for the electrodes were purchased from Niraco Co., Ltd. (Tokyo).

Figures 2 a) and b) show the current vs. voltage (I vs. V) curve and FFT of the output current, respectively, for Sample A. In this figure, the results with 1) the platinum electrode, 2) the carbon electrode, and 3) the silver electrode are given. The I vs. V curves for the different drinks are markedly different from each other. It is also noted that the

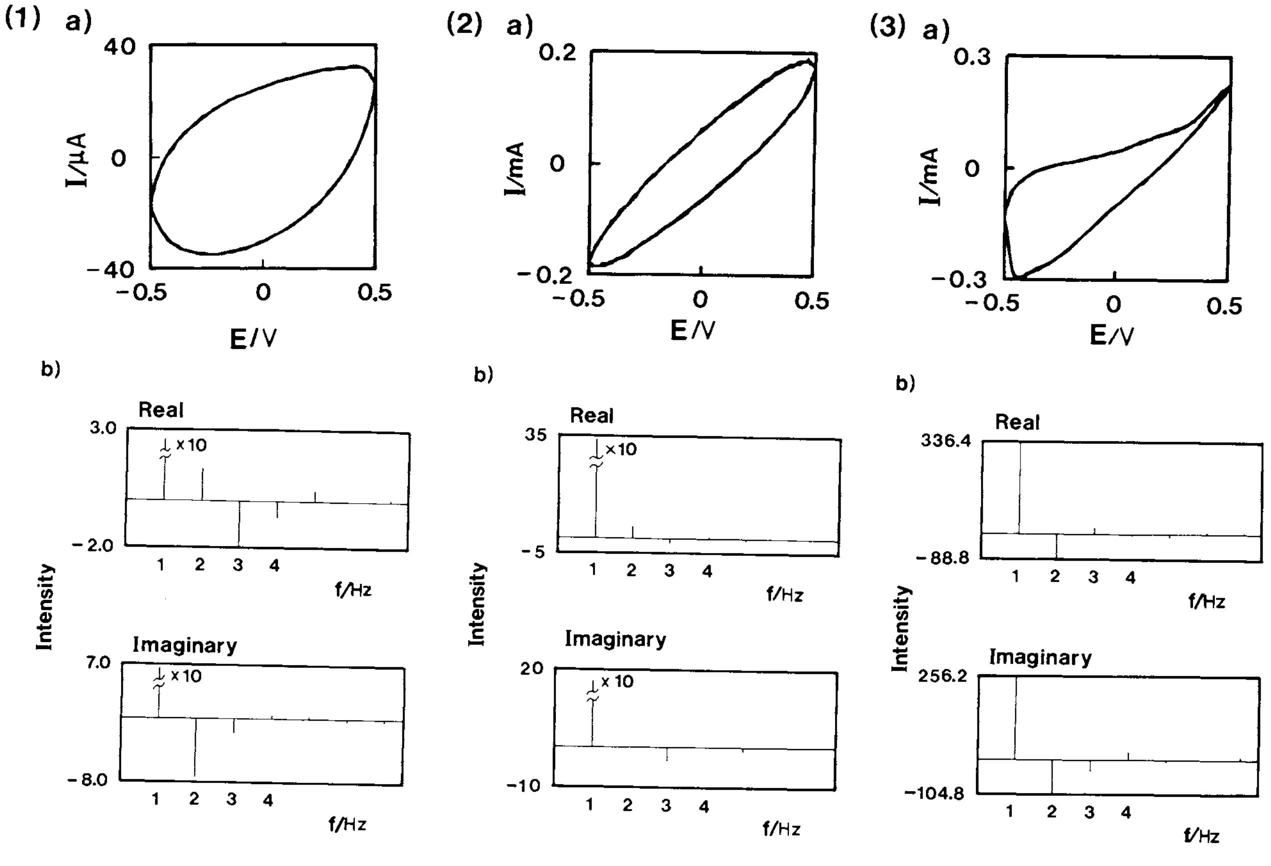

Fig. 2. Characteristic response for sample A (can coffee).
a) current-voltage curve and b) FFT upon the current wave of a).
1) platinum, 2) carbon, and 3) silver electrodes.

difference of the I vs. V curves is dependent on the nature of the metal electrode. In order to analyze the characteristics of the I vs. V curves quantitatively, the time-trace of the output current was Fourier transformed to the frequency domain (Fig.2-b). Here, the real and the imaginary parts at the fundamental frequency (1 Hz) correspond to the conductance and the capacitance, respectively. The intensities of higher harmonics are concerned with the nonlinearity of the system. The reproducibility of the relative intensity of the higher harmonics is quite good. The experimental errors are below 5 percent for the electrode for even after more than one week.

In order to clarify the relationship between the intensities of the higher harmonics and the electrochemical nonlinearity, let us now discuss the relationship between the intensities of the higher harmonics and the nonlinearity of capacitance or conductance.1) The nonlinear property of the capacitance and conductance is generally given by the following equations,

$$C(V) = C_0 + C_1V + C_2V^2 + C_3V^3 + \cdots \tag{1}$$

$$G(V) = G_0 + G_1V + G_2V^2 + G_3V^3 + \cdots \tag{2}$$

When a sinusoidal voltage ($V = E_1 \sin \omega_0 t$) is applied to a system of parallel circuits with a nonlinear capacitor and a nonlinear resistor, the output current, I(t), is given as the summation of capacitance, $I_C(t)$, and conductance, $I_G(t)$, components.

$$\begin{aligned} I(t) &= I_C(t) + I_G(t) \\ &= (C_0 + \frac{C_2E_1^2}{4})\omega_0 E_1 \cos \omega_0 t - \frac{C_2E_1^3\omega_0}{4} \cos 3\omega_0 t \\ &\quad + (\frac{C_1}{2} + \frac{C_3E_1^2}{4})\omega_0 E_1^2 \sin 2\omega_0 t - \frac{C_3E_1^4\omega_0}{8} \sin 4\omega_0 t \\ &\quad + \frac{E_1^2}{2}(G_1 + \frac{3G_3E_1^2}{4}) + E_1(G_0 + \frac{G_2E_1^2}{4}) \sin \omega_0 t \\ &\quad - \frac{E_1^2}{2}(G_1 + G_3E_1^2) \cos 2\omega_0 t + \frac{G_3E_1^4}{8} \cos 4\omega_0 t - \frac{3G_2E_1^3}{4} \sin 3\omega_0 t \end{aligned} \tag{3}$$

Equations 1, 2, and 3 indicate that one can evaluate the nonlinear properties of capacitance and conductance separately from the the higher harmonic components. Using Eqs. 1-3 and the experimental results of FFT on the output current, we performed a simulation of the nonlinearity of the capacitance (Fig.3-1) and conductance (Fig.3-2). The characteristic responses for the various drinks indicate that these may be distinguished based on the information of nonlinear characteristics with several electrodes.

At the present time, results obtained by this novel method of chemical sensing are only preliminary. However, as the present method affords us abundant information on the electrochemical processes, it may become possible to distinguish and to quantify various chemical compounds present in the test solution. The algorithm developed by Hopfield for the neural computer may serve as a powerful tool for analysis of a multi-variable system.$^{3)}$ We intend to initiate a study designed to utilize the 'neural-computer' for development of the chemical sensing system reported herein. It should also be noted that this method is excellent and useful both with respect to ease of handling and reproducibility. We have recently reported$^{1)}$ that taste compounds characteristically change the nonlinear capacitance of an electrochemical system depending on the taste-categories they belong.

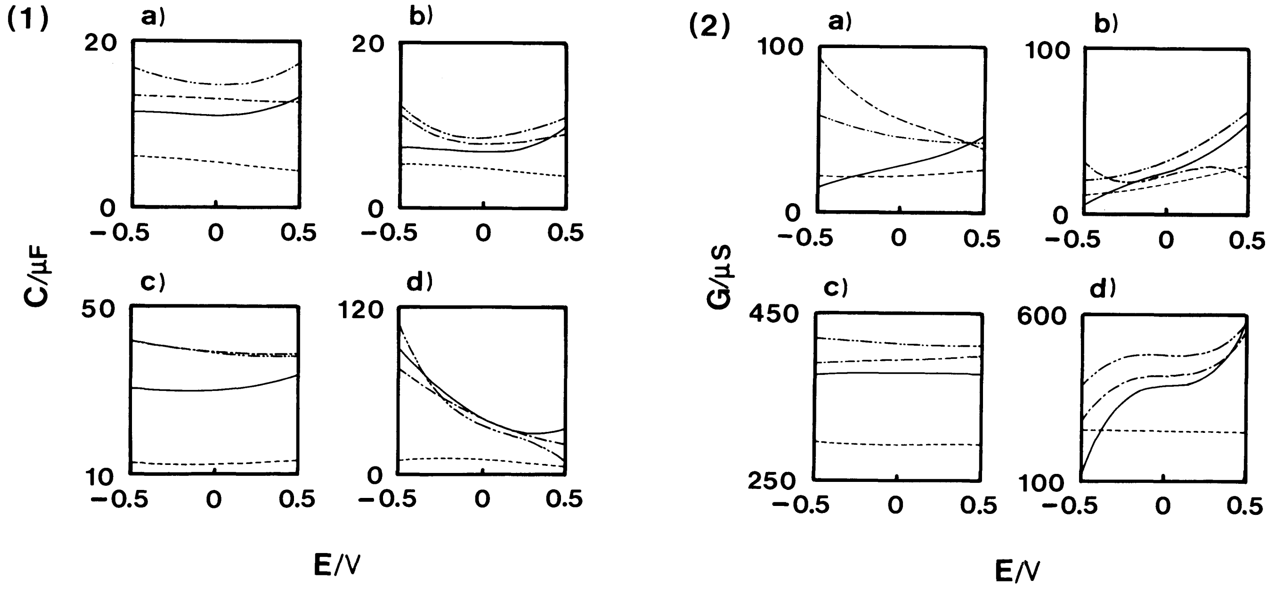

Fig. 3. Simulated voltage-dependent capacitance (1) and resistance (2) deduced from FFT of current wave.
a) platinum, b) gold, c) carbon, and d) silver electrodes.
——: Sample A, ------: Sample B, —·—·—: Sample C, —··—: Sample D

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