Fabrication of an Integrated Square Wave Voltammetry (SWV)-Redox Sensor

Byounghyun Lim¹, Masato Futagawa², Sou Takahashi¹, Fumihiro Dasai^{1,3}, Makoto Ishida^{1,4}, Kazuaki Sawada^{1,3,4}

¹ Department of Electrical and Electronic Information Engineering, Toyohashi University of Technology

1-1 Hibarigaoka, Tempaku-cho, Toyohashi, Aichi 441-8580, Japan

Phone: +81-532-44-6728 E-mail: bhlim@int.ee.tut.ac.jp

² Head Office for "Tailor-Made and Baton-Zone" Graduate Course, Toyohashi University of Technology

1-1, Hibarigaoka, Tempaku-cho, Toyohashi, Aichi 441-8580, Japan

³ Core Research for Evolutional Science and Technology, Japan Science and Technology Agency

7, Gobancho, Chiyoda-ku, Tokyo 102-0076, Japan

⁴ Electronics-Inspired Interdisciplinary Research Institute (EIIRIS), Toyohashi University of Technology

1-1, Hibarigaoka, Tempaku-cho, Toyohashi, Aichi 441-8580, Japan

Abstract

An integrated square wave voltammetry (SWV) redox sensor has been developed on a 5 x 5 mm² Si chip. The sensor consists of a SWV pulse generator, a voltage controller, and two electrodes for electrochemical analysis. Our proposed sensor is the first integrated sensor system of SWV pulse generator. Potassium ferricyanide solution was measured to obtain characteristics of proposed sensor. We confirmed that the dynamic range of concentration and frequency was obtained from 0.6 to 6 mM and from 20 to 500 Hz of potassium ferricyanide.

1. Introduction

In a field of biological and medical science, electrochemical sensors have been attracting attention for biomaterial analysis. ISFET-type biosensor is mainly used to detect protein or enzyme such as glucose, penicillin, and albumin which are significant materials to human body [1]. This type of sensor is possible to detect only one kind of biomaterial with one sensing area. In contract, the redox sensors can monitor various materials with the same sensing area at the same time. The integrated redox sensors for miniaturizing sensor system had been fabricated with cyclic voltammetry circuits which is widely used in many fields [2,3]. However, fast scanning measurements using the cyclic voltammetry cannot be operated because of an influence of charge currents on electric double layer capacitance. Therefore, these conventional sensors had been taken a few minutes to scan. On the other hands, SWV method is capable of increasing the scan rate without raising the capacity current [4].

In this study, we proposed and fabricated a SWV redox sensor integrated the novel SWV pulse generator, the sensing electrodes which were a working electrode (WE), a counter electrode (CE), and a voltage controller circuit on the 5 x 5 mm² Si chip. The SWV pulse generator was designed to adjust the scan rate, the scan range, and the start voltage of the scan for its purposes.

2. Experimental Procedure

Design of SWV Pulse Generator

Integrated SWV pulse generator consists of presetter, counter, selector, D flip flop, 8-bit DAC, and voltage shifter as shown in Fig. 1. We can modulate the step height, amplitude, and frequency of SWV pulse using reference voltage, presetter, and system clock, respectively.







Fig. 2. A photograph of the sensor chip

Overview of the system

Figure 2 shows the entire photograph of the sensor chip. The SWV pulse enters the CE through voltage controller. An external Ag/AgCl reference electrode in KCl solution is connected with sensor to monitor the potential of solution. The output current flows at WE, which is 500 x 500 μ m², when SWV pulse is entered the solution. Then, we can measure the output voltage through an external current-voltage converter. Potassium ferricyanide solution was measured to obtain characteristics of proposed chip.

3. Results

Figure 3(a) is an output voltage signal from the SWV pulse generator. This waveform is a good match with general SWV pulse [4]. The SWV pulse enter the potentiostat. Then, we can see the output current from the WE as shown in Fig. 3(b). We can obtain the current characteristics from a differential value between reduction and oxidation current and can also obtain kind of materials by its redox potential as shown in Fig. 3(c). Figure 4 is a comparison of a peak current between potassium ferricyanide and potassium chloride. Potassium ferricyanide has its peak current depends on concentration, but potassium chloride does not have it. From this result, we can verify that the proposed sensor can detect potassium ferricyanide.



Fig. 3. (a) Output voltage signal of SWV pulse. (b) Reduction-oxidation current response and (c) current-voltage plot of potassium ferricyanide.



Fig. 4. Comparison of peak current between potassium ferricyanide and potassium chloride.

Figure 5(a) shows the SWV frequency dependence of a peak faraday current, and Fig. 5(b) shows the potassium ferricyanide concentration dependence of the peak faraday current. The peak faraday current is a subtracted net peak current from capacity current. This sensor showed a strong linearity in the plots of the peak faraday current versus square root of SWV frequency with an accuracy over 96% and in the plots of the peak faraday current versus concentration with an accuracy over 99% at the range of 0.6 to 6 mM and 20 to 500 Hz, respectively.



Fig. 5. (a) SWV Frequency dependence of the peak faraday current. (b) Potassium ferricyanide concentration dependence of the peak faraday current.

4. Conclusions

An Integrated SWV redox sensor chip was designed and fabricated. We can control the system speed and the range of input signal employing this chip as its purposes. This sensor also shows a good linearity at the range of 0.6 to 6 mM and 20 to 500 Hz. Owing to its controllable system, proposed sensor chip might be apply other devices and other biomaterials.

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