Note

A Novel Data Acquisition Method for Visualization of Large pH Changes by Chemical Imaging Sensor

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A chemical imaging sensor is a semiconductor device that can visualize the pH distribution in a solution. In the conventional constant-bias method, in which a photocurrent map is converted into a pH image, the measurable range of pH values is rather limited and the result is interfered by the impedance of the solution. In this study, a novel method of data acquisition and image construction is proposed, which can measure a larger pH change without interference of the impedance.

KEY WORDS: chemical imaging sensor; LAPS; pH distribution.

1. Introduction

A pH value is one of the most fundamental indices in electrochemistry. Our group has been engaged in the development of chemical imaging sensor systems,^{1,2)} which can visualize the spatial distribution of pH values in a solution. It is based on the principle of the light-addressable potentiometric sensor (LAPS),³⁾ which utilizes a scanning laser beam to read out the field-effect-induced distribution of carriers in a semiconductor.

In addition to the various fields of its prospective applications in chemistry and biology, the chemical imaging sensor is also useful for investigation of corrosion^{4,5)} and hydrogen permeation in steel. We are preparing a setup to observe the distribution of protons after permeation of hydrogen through a steel plate.

In a LAPS measurement, an ac photocurrent signal is obtained as a function of the bias voltage applied to the sensor. The horizontal shift of the photocurrent–voltage curve along the voltage axis can be correlated with the pH value by the Nernstian equation. The shift of the curve is usually characterized by the displacement of its inflection point, which is determined either by calculating the second derivative or equivalently by fitting the vicinity of the inflection point with a cubic function. In the case of imaging, however, it is too time-consuming to acquire the photocurrent–voltage curves at all pixels, especially when the number of pixels is large. In a conventional method, therefore, the bias voltage

is fixed at a single value during the scan and the photocurrent values are collected at all pixels. After the measurement, the photocurrent values are converted into the voltage shift by assuming a linear slope of the transition region of the photocurrent–voltage curve.

The conventional method, however, has two problems. Firstly, the linear part of the photocurrent–voltage curve is limited and the photocurrent value saturates at its maximum or minimum for a large change of pH. Secondly, the amplitude of the ac photocurrent is interfered by the local impedance of the solution, while the shift of the photocurrent–voltage curve is not interfered.

In this note, a novel method of data acquisition and image construction for a chemical imaging sensor system is proposed. In this method, a relatively small number of scans are conducted at different bias voltages to obtain a series of photocurrent images. The shift of the photocurrent–voltage curve at each pixel is then determined by curve fitting to construct a pH image. It is demonstrated that the proposed method can visualize a large pH change, which would be useful, for example, in a study of metals.

2. Experimental

2.1. Measurement System

Figure 1 shows a schematic view of the chemical imaging sensor. The measurement system is intrinsically the same as described in our previous papers.^{6,7)} It consists of a sensor plate made of n-type silicon with an insulating layer, optics for laser scanning and measurement electronics.

2.2. Acquisition of Photocurrent Images

A series of photocurrent images (32×32 pixels) were acquired at 15 or 27 different bias voltages with a variable step of 20 to 100 mV, so that the total range of the bias voltage included the transition region of the photocurrent–voltage curve. The photocurrent data was then rearranged into 32×32 photocurrent–voltage curves, each of which consisted of 15 or 27 data points with a separation of 20 to 100 mV.

2.3. Curve Fitting

In the conventional detection method of a potential shift in a LAPS, a high density of data points on the photocurrent–voltage curve is necessary to calculate the local curvature and to determine the inflection point pre-

Fig. 1. Schematic view of the chemical imaging sensor system.

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cisely. In the novel method proposed in this study, the potential shift is determined with a smaller number of data points by looking at the global shape rather than the local curvature of the photocurrent–voltage curve. The shape of photocurrent–voltage curve reflects the bias state of the sensor. The photocurrent increases as the sensor is depleted, and saturated in the region where the sensor is in the inversion state. Then the photocurrent–voltage curve is fitted with a logistic function model:

$$y = \frac{y_0}{1 + e^{-a(x-x_0)}}, \dots\dots\dots (1)$$

where three fitting parameters of x_0 , y_0 and a represent the horizontal location of the inflection point, the vertical height of the curve and the slope of the transition region, respectively. A collection of x_0 gives a potential map, which can be further converted into a pH map by using the pH sensitivity value of the sensor plate.

3. Result and Discussion

Figure 2 shows an example of photocurrent–voltage curves for standard pH buffer solutions of pH 7, pH 5 and pH 2. A horizontal shift of the curve depending on the pH value is observed. As shown in the inset, the linear part of the pH 7 curve ranges from -0.95 V to -0.67 V, only within which the photocurrent changes linearly with pH. The slope of the linear part was -44.2 nA/V.

3.1. Constant-bias Method

Figure 3(a) shows the photocurrent map obtained at a constant bias voltage of -0.80 V for a pH 7 buffer solution. **Figures 3(b) and 3(c)** show the photocurrent difference at each pixel for pH 5 and pH 2, respectively, with respect to the values for pH 7. Two additional scales are shown, which convert the photocurrent difference into the potential difference and pH, respectively. The higher limit, -0.67 V, of the linear part of the pH 7 curve in **Fig. 2** corresponds to a potential difference of $+130$ mV with respect to the bias point of -0.80 V, which further corresponds to a pH change of -2.2 , and therefore, a pH value of 4.8 . From this estimation, therefore, pH values below 4.8 cannot be correctly determined by the constant-bias method. In fact,

the average values in **Figs. 3(b) and 3(c)** correspond to pH 5.1 and pH 3.8 , respectively, even though pH 5 and pH 2 solutions were measured.

3.2. Curve-fitting Method

Figure 4 shows an example of curve fitting, in which data points for pH 7, pH 5 and pH 2 at the same pixel are fitted with logistic functions. The number of data points are 27 for pH 7 and 15 for pH 5 and pH 2. Although the reason why the photocurrent gradually increased in inversion state is not clear, the data points are smoothly fitted with logistic functions, which suggests that the horizontal displacement can be correctly determined with such sparse sets of data points.

Figure 5(a) shows a map of the parameter x_0 or the bias voltage corresponding to the inflection point of the logistic

Fig. 3. Photocurrent images obtained by the conventional constant-bias method for (a) pH 7 (b) pH 5 and (c) pH 2. (Online version in color.)

Fig. 2. Photocurrent–bias voltage curves for different pH values.

Fig. 4. Curve fitting of data points at the same pixel with a logistic function for pH 7, pH 5 and pH 2.

curve obtained by fitting data points for pH 7 at each pixel. Figures 5(b) and 5(c) show the maps of the potential difference at pH 5 and pH 2 with respect to pH 7. Additional scales are also shown, which convert the potential difference

into pH values.

The average values in Figs. 5(b) and 5(c) correspond to pH 4.9 and pH 1.8, respectively, which proves that the proposed curve-fitting method can follow a larger shift of the photocurrent–voltage curve and therefore can measure a larger pH change in comparison to the conventional constant-bias method.

4. Conclusions

In this study, a novel method of data acquisition and image construction for a chemical imaging sensor system was proposed. A relatively small number of data points per pixel are fitted with a logistic function to determine the shift of the photocurrent–voltage curve and to determine the pH value. Compared to the conventional constant-bias method, the proposed curve-fitting method could measure a larger change of pH, which would be useful for a study of metals.

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Fig. 5. Potential images obtained by the proposed curve-fitting method for (a) pH 7 (b) pH 5 and (c) pH 2. (Online version in color.)