Detection of Hydrogen Permeation through Pure Iron with Light-addressable Potentiometric Sensor

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A light-addressable potentiometric sensor (LAPS) is a semiconductor-based chemical sensor, in which the measurement area is defined by a probe light illuminating the sensor plate. In this study, a novel method to detect hydrogen permeation through metal was proposed using a measurement system, in which a LAPS was combined with a micro-volume measurement cell. The sensing surface of the LAPS was placed in the vicinity of the hydrogen exit surface of an iron sheet to form the micro-volume cell. The cell was filled with a Na$_2$HPO$_4$ solution, and then the pH change of the solution due to production of protons during the electrochemical hydrogen permeation was detected. After loading hydrogen atoms from the hydrogen entry side into the iron sheet, the photocurrent – bias voltage characteristics of the LAPS showed a shift indicating production of protons. The result suggested the possibility of applying the LAPS to visualization of hydrogen permeation sites on the metal surface.

KEY WORDS: chemical sensor; hydrogen permeation; Devanathan-Stachurski cell.

1. Introduction

Chemical sensors play important roles in the fields of chemistry, materials science and medicine as well as in industry. Especially, chemical sensors based on the field effect in semiconductor (e.g. ion-sensitive field-effect transistor, IS-FET) have been widely used to evaluate the ion concentrations in various samples. The light-addressable potentiometric sensor (LAPS)1) is a unique variant of semiconductor-based chemical sensors with an advantage of spatially-resolved measurement. Figure 1 shows the configuration of a LAPS and its measurement system. The sensor plate is made of silicon with insulator layers on its surface and has ohmic-contact electrodes on its backside. The measurement system consists of the sensor plate, a measurement cell, a modulated light source and electronics for acquisition of signals. In LAPS measurement, a DC bias voltage $V_{bias}$ is applied to the sensor plate with respect to the reference electrode and a modulated light illuminates the backside of the sensor plate to induce an AC photocurrent. Then the amplitude of the AC photocurrent is recorded as a function of the bias voltage. The pH value of the solution in contact with the sensing surface can be determined by measuring the shift of the photocurrent – bias voltage characteristic ($I$–$V$ curve), which reflects the Nernstian response of the sensing surface with a sensitivity of about 59 mV/pH.2)

Using a scanning light beam, the LAPS principle has also been applied to chemical imaging, which visualizes the spatial distribution of the ion concentration on the sensing surface.3,4) This technique has been applied to various electrochemical systems as well as biological samples. Examples of the former include pH distribution during electrolysis5) and corrosion,6–8) and examples of the latter include metabolic activity of bacteria,9–11) enzymatic activity,12,13) and defects in a cultured cell layer.14)

In this paper, we propose a novel application of LAPS in the detection of hydrogen permeation through an iron sheet in a Devanathan-Stachurski cell.15) The sensing surface of a LAPS was placed in the vicinity of the anode surface of the iron sheet and the production of protons by the oxidizing current was detected in the form of a pH change.

2. Experiment

Sample preparation: A pure iron sheet (purity: 99.5 mass%, thickness: 0.25 mm, The Nilaco Corporation, Tokyo Japan) was cut into 12 mm × 13 mm, and one side of the iron sheet was polished by waterproof abrasive papers with grit sizes of P400, P600, P800, P1000, P1500 and P2000 in this order. The polished surface was then chemically etched

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for 5 min in a mixture of 19 mL of 30% H$_2$O$_2$ (FUJIFILM Wako Pure Chemical Corporation, Osaka, Japan), 1 mL of 46% HF (Morita Chemical Industries Co. Ltd., Osaka, Japan) and 20 mL of deionized water, which reduced the thickness of the iron sheet by about 30 $\mu$m. The etched surface was immediately palladium-plated at a constant current density of 0.96 mA/cm$^2$ for 90 min (K-pure palladium series, Kojima Chemicals Co. Ltd., Saitama, Japan). During the processes of etching and plating, the other side of the iron sheet was protected with an adhesive polyimide tape (AS ONE Corporation, Osaka, Japan). The thickness of the palladium layer was estimated to be 2.4 $\mu$m.

Measurement system: The sensor plate and the data acquisition system were intrinsically the same as those used in our previous studies. A home-made electronic circuit was developed, which functions (1) as a bipotentiostat to simultaneously control the potentials of both the iron sheet and the LAPS sensor plate, (2) as a bipotentiostat to maintain the polarization potentials on both sides of the iron sheet during hydrogen charge, and (3) as a preamplifier with a gain of 10$^7$ V/A to detect the AC photocurrent signal of the LAPS.

Micro-volume cell: Fig. 2 shows configurations of the measurement systems. As shown in Fig. 2(a), the iron sheet was fixed on the LAPS sensor plate with two layers of double-sided tapes (#9965, 3M Company, Minnesota, U.S.), so that the sensing surface of the LAPS faced the palladium-plated surface with a distance of 0.17 mm. A micro-volume cell with a capacity of 11 $\mu$L was formed between the iron sheet and the sensing surface, and the cell was connected via a salt bridge to a reservoir to accommodate the Ag/AgCl reference electrode (RE-1B, BAS Inc., Tokyo, Japan) and the counter electrode (Pt wire). Hydrogen atoms were extracted into this micro-volume cell in the form of protons under a potentiostatic condition and the resultant pH change was detected.

3. Results and Discussion

The iron sheet was then set as shown in Fig. 2(a) and the micro volume was filled with 0.1 M Na$_2$HPO$_4$ (pH 9). In advance of the measurement, the native hydrogen atoms in the iron sheet were sufficiently extracted from the palladium-plated surface by over 12 hours of potentiostatic polarization at +100 mV vs Ag/AgCl. After that, the measurement cell was refilled with fresh 0.1 M Na$_2$HPO$_4$ again.

At the beginning of the measurement, the iron sheet was polarized at +100 mV vs Ag/AgCl from 0 to 65 min in the configuration shown in Fig. 2(a) and $I$-$V$ curves were collected with an interval of 10 min. Second, hydrogen atoms were loaded into the iron sheet from the top side using the configuration shown in Fig. 2(b). The hydrogen entry surface was contacted with a solution containing 3% NaCl and 3 g/L of NH$_4$SCN. From 65 to 125 min (60 min), the hydrogen entry surface and hydrogen exit surface were polarized at −1.0 V and +100 mV vs Ag/AgCl, respectively. Finally, after the entry of hydrogen atoms, the configuration was switched back to Fig. 2(a), and the iron sheet was polarized again at +100 mV from 125 to 190 min (65 min).

The current profiles during the hydrogen loading and extraction are shown in Figs. 3(a) and 3(b), respectively.

![Fig. 2. Configurations of the system for (a) hydrogen extraction and pH measurement by the LAPS and (b) hydrogen loading.](image-url)

![Fig. 3. Current profiles of (a) hydrogen loading and (b) hydrogen extraction.](image-url)
The hydrogen extraction current increased with a delay of 1 min after starting the hydrogen loading, and the maximum value of that was about 5.8 μA. The temporal change of the pH value in the micro-volume cell was monitored by collecting I–V curves. Two series of I–V curves before and after the hydrogen loading are shown in Fig. 4. The data collecting time of an I–V curve and the interval of the measurement were 4 min and 10 min, respectively. While the first series of I–V curves before hydrogen loading overlapped each other and did not show obvious shift, a large horizontal displacement was plotted in Fig. 5. Two series of I–V curves were collected before hydrogen loading overlapped each other. (Online version in color.)

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The temporal change of the inflection point is expected in the future study.

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