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Response characteristics of all-solid-state pH sensor using $Li_5YSi_4O_{12}$ glass

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Abstract

A new type of all-solid-state pH sensor was investigated for the monitoring of pH in high temperature. The all-solid-state pH sensor consists of two half-cells: indicator electrode using the $Li_5YSi_4O_{12}$ glass and an Ag/AgCl reference electrode coated with Nafion film. A stable Nafion film was achieved by heat treating at 100 °C for 1 h. The electromotive force (EMF) of the all-solid-state pH sensor decreased linearly with pH increase in water in accordance with the Nernst's equation. The all-solid-state pH sensor operated stably up to 80 °C. The sensitivity of the all-solid-state pH sensor against pH was high, and the EMF was also scarcely influenced by the presence of inorganic ions such as Li^+, Na^+ and Cl^-. It was practically confirmed by the pH titration test that the all-solid-state pH sensor behaved similar to the commercial pH meter with the conventional glass electrode. In addition, the all-solid-state pH sensor showed same equivalence point both at high temperature and low temperature operations.

Keywords: C. Electrical properties; C. Ionic conductivity; E. Electrodes

1. Introduction

Measurement of hydrogen ion concentration (pH) is important in a wide range of fields for the clarification of chemical properties of materials and for the management of chemical reaction. Generally, pH meters employing the glass electrode and the Ag/AgCl, Cl^--electrode are used. It has some issues such as weakness of physical strength since the glass electrode consists of thin glass membrane, and troublesome maintenance since the glass membrane must be dipped in water all the time. Miniature pH electrode is in demand for a medical application to measure the pH of stomach fluid. Currently, combined electrode which is integrated with glass electrode, reference electrode and temperature compensated electrode is used. Although this type of combined pH sensor became compact, it has limitation in miniaturization of electrode part for the conventional liquid membrane type electrode using electrolyte solution. In order to downsize the pH sensor part, the whole part (indicator electrode and reference electrode) is needed to be all-solid-state electrode. There are some reports about the all-solid-state pH sensor using ceramics as indicator electrode [1–3]. In addition, other all-solid-state pH sensors are introduced by Vonau and Guth [4].

Therefore, this study aimed to develop a new type of miniature all-solid-state pH sensor that consisted of solid-state reference electrode and solid-state indicator electrode, which does not require electrolyte solution and salt bridge. The all-solid-state pH sensor was prepared by combining the $Li_5YSi_4O_{12}$ glass (pH indicator electrode), which was reported as Li^+ ion conductor, and an Ag/AgCl electrode (reference electrode) coated with Nafion film. [5,6] Meanwhile it was already reported that this type of all-solid-state pH sensor showed good response characteristics at room temperature operation [7]. In this study, we additionally investigated whether this type of all-solid-state pH sensor works or not at high temperature range (up to 80 °C).

2. Experimental

The preparative procedure of the $Li_5YSi_4O_{12}$ glass is as follows. Reagent grade Li_2CO_3 and SiO_2, and Y_2O_3 were used for the starting materials. After mixing in the molar ratio of

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Li_2CO_3:Y_2O_3:SiO_2 = 35.7:7.2:57.1, the mixture was melted in a platinum melting crucible at 1350 °C for 1 h in an air atmosphere using an electric furnace. The melted was quenched on the iron plate and molded with pressing. The $Li_5YSi_4O_{12}$ glass was obtained by annealing at 400 °C in order to prevent the distortion and crack. The formation of glass was confirmed by the powder X-ray diffraction analysis (XRD, Rigaku MiniFlex). The conductivity was measured in the temperature range of 200–400 °C and the frequency range of 100 Hz to 10 MHz with an impedance analyzer (HP4194A), using the 5 mm × 5 mm × 1 mm shaped sample with putting Ag electrodes on both sides.

Schematic view of the all-solid-state pH sensor (the half cell (I): reference electrode and the half cell (I): indicator electrode) was shown in Fig. 1. As for the half cell (I), a proton-conductive Nafion film was formed by dip coating an Ag/AgCl electrode in Nafion® solution (Aldrich, 20 wt% solution) and drying at 100 °C for 1 h under an atmosphere of air. In the obtained Nafion film, it is guessed that the (–CF_2–CF_2–) links are almost maintained. However, it is thought that a part of –SO_3H has been decomposed [8]. Therefore, the resistance of the Nafion film was a high value (600 kΩ, thickness: 0.18 mm). As for the half cell (II), a Pt wire was attached onto a side of the $Li_5YSi_4O_{12}$ glass disc (Φ 10 mm × t 1 mm) with silver paste, and another side of the glass disc was directly mounted on a glass tube with epoxy resin (see Fig. 1), and then it was dried at 100 °C for 1 h. The following half cells were set up to measure the dependence of electromotive force (EMF) of each cell on pH at 25 °C. The saturated KCl solution was used in the conventional Ag/AgCl, Cl^--electrode. An electrometer (Advantest TR8652, input impedance > 10^{13} Ω) was used to measure the electromotive force. The pH adjustment of sample solutions was done using HCl and NaOH solutions.

$$\text{conventionalAg/AgCl, Cl}^-\text{-electrodevs.halfcell(I)} \quad (1)$$

$$\text{conventionalAg/AgCl, Cl}^-\text{-electrodevs.halfcell(II)} \quad (2)$$

As for the all-solid-state pH sensor, half cells (I) and (II) were combined to set up the following cell, and dependence of EMF on pH at 25–80 °C was measured.

$$\text{halfcell(I)vs.halfcell(II)} \quad (3)$$

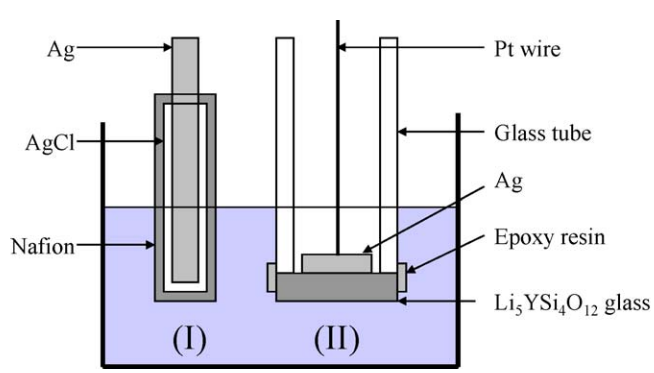

Fig. 1. Schematic view of the all-solid-state pH sensor. half cell (I):Ag/AgCl reference electrode coated with Nafion film and, half cell (II):indicator electrode using the $Li_5YSi_4O_{12}$ glass disc.

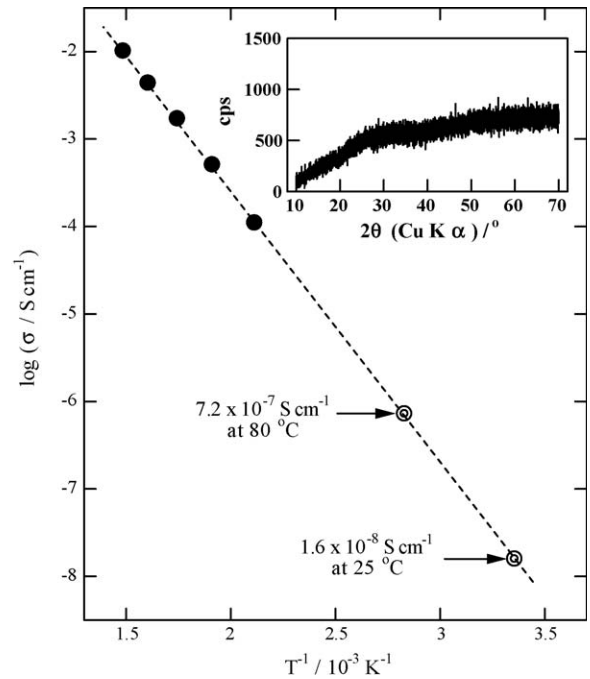

Fig. 2. XRD pattern and temperature dependence of conductivity for the $Li_5YSi_4O_{12}$ glass.

3. Results and discussion

From the XRD result at the room temperature shown in Fig. 2, only a halo pattern near $2\theta = 30°$ was observed for the prepared disc, and no other diffraction peaks attributable to the crystalline phases were recognized. This result suggests that the prepared $Li_5YSi_4O_{12}$ is glass (amorphous). The resistance at 25 °C and 80 °C of the $Li_5YSi_4O_{12}$ glass is guessed to be about 6.3×10^7 Ω cm and 1.4×10^6 Ω cm, respectively, from the conductivity at 200–400 °C shown in Fig. 2.

Dependence of EMF of the cells (1) and (2) on pH was shown in Fig. 3. The EMF of the cell (1) was almost independent of pH in water, and showed a steady value. This suggests that membrane potential did not generate at the surface of the Nafion film. Accordingly it showed that this Nafion film is just a proton conductive membrane and it worked as a protective membrane for the Ag/AgCl electrode. From this fact, it can be considered that the Ag/AgCl electrode coated with Nafion film can be used as a reference electrode against pH. Here, it is thought that the inside of the Ag/AgCl/Nafion reference electrode is saturated solution of AgCl because the Nafion film slightly passes water. The Cl^- concentration is guessed to be about 10^{-5} mol/l. In contrast, the EMF of the cell (2) decreased linearly with an increase of pH in water in accordance with the Nernst's equation. This suggests that the indicator electrode using $Li_5YSi_4O_{12}$ glass worked as a pH sensitive electrode. The all-solid-state sensor shown in Fig. 1 does not require the use of salt bridge, and it is designed to measure pH in only one solution. These facts, without the need of salt bridge and electrolyte solution, greatly differ from the conventional glass electrode. Dependence of EMF of the cell (3) on pH was also shown in Fig. 3. The EMF decreased linearly with an increase of pH in water. In this way,

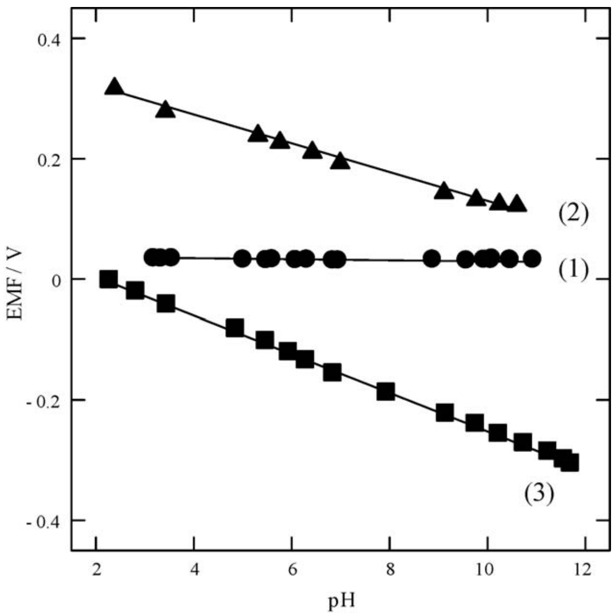

Fig. 3. Dependence of electromotive force (EMF) of the cells ((1) and (2)) and the all-solid-state pH sensor (3) on pH in the aqueous solution at 25 °C. (1) Conventional Ag/AgCl, Cl^--electrode vs. half cell (I) in Fig. 1, (2) conventional Ag/AgCl, Cl^--electrode vs. half cell (II) in Fig. 1, (3) half cell (I) vs. half cell (II).

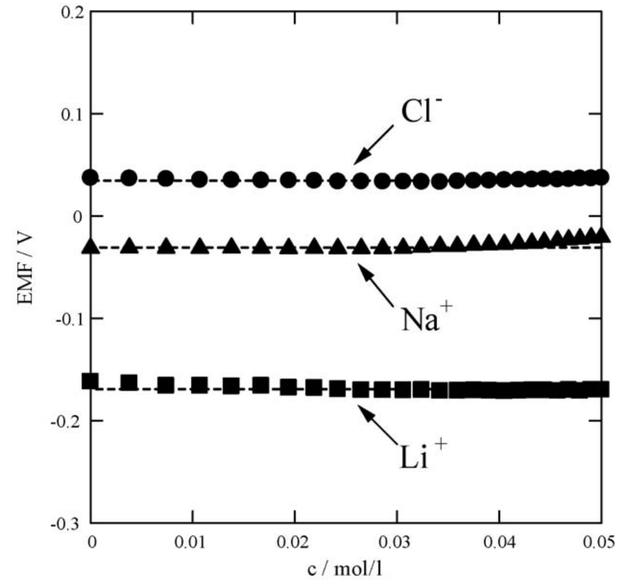

Fig. 4. Influence of addition of electrolyte concentration (c) in EMF of the all-solid-state pH sensor at 25 °C.

dependence of EMF of the all-solid-state sensor on pH was also confirmed. A potential (E) of pH glass electrode in hydrogen ion containing solution can be expressed as the following Nernst's equation.

$$E = E^0 - \left(\frac{2.303RT}{F}\right)\text{pH}$$

where, E^0, R, T, and F are standard potential, gas constant, absolute temperature, and Faraday constant, respectively. In this equation, electrode potential and pH are in linear relationship, and the slope of the straight line is −2.303RT/F. Accordingly, it can be seen that the potential (E) will shift to negative direction by 59.16 mV at every time pH increases 1 unit. However, actually abnormal phenomenon occurs when pH is higher than 10 in the use of a glass electrode. In conventional glass electrode, the linearity of glass electrode as a hydrogen ion electrode is lost in alkali solution with higher than pH 10, and the indicator shows moderately acidic than a hydrogen electrode, and it is called ''alkali error''. But the all-solid-state pH sensor showed linear decrease even at the pH levels higher than 10. It was considered that alkali error can be suppressed by using the $Li_5YSi_4O_{12}$ glass.

The experimental results of the influence of inorganic ions such as Cl^-, Na^+ and Li^+ ions on the EMF of the cell were shown in Fig. 4, and it was found that the EMF of the cell was almost independent of the increase of such ions in the water. It was revealed that the all-solid-state pH sensor using the $Li_5YSi_4O_{12}$ glass has higher selectivity for H^+ ion without the influence of other anions and cations.

In order to examine the pH response mechanism of the EMF, an interface model of solid electrolyte ($Li_5YSi_4O_{12}$ glass) and solution is proposed as follows. It is thought that a small amount of Li^+ ion in the $Li_5YSi_4O_{12}$ glass elutes in the solution, and a part of Li^+ ion has been exchanged for H^+ in the vicinity of the interface. The H^+ ions at the lattice points can have relationship electrically with the H_3O^+ ions in the solution. Basing on this consideration, it can be explained that the EMF of the half cell using the $Li_5YSi_4O_{12}$ glass depends upon pH.

Temperature dependence of the all-solid-state pH sensor was examined by measuring the EMF of the cell in pH 4.0 and pH 9.0 solutions in the temperature range from 25 °C to 80 °C at 5 °C interval, and the measurement results were shown in Fig. 5. (The pH shown in Fig. 5 was a value at 25 °C. The temperature of the solution was raised and the EMF was

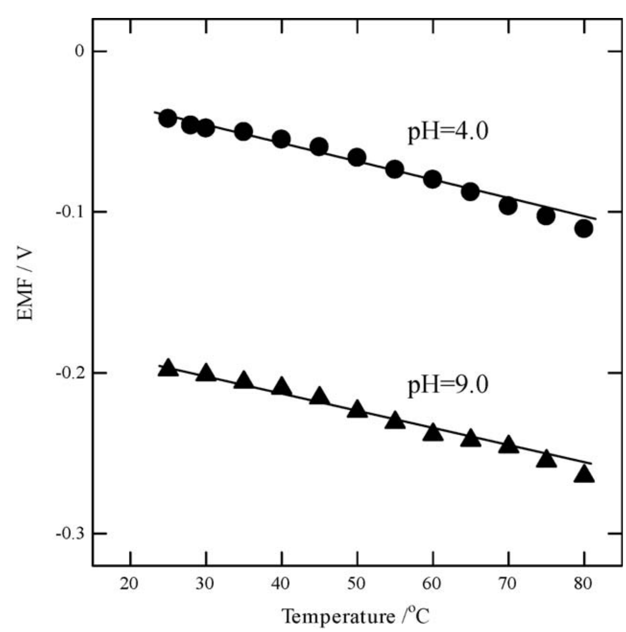

Fig. 5. Temperature dependence of EMF of the all-solid-state pH sensor.

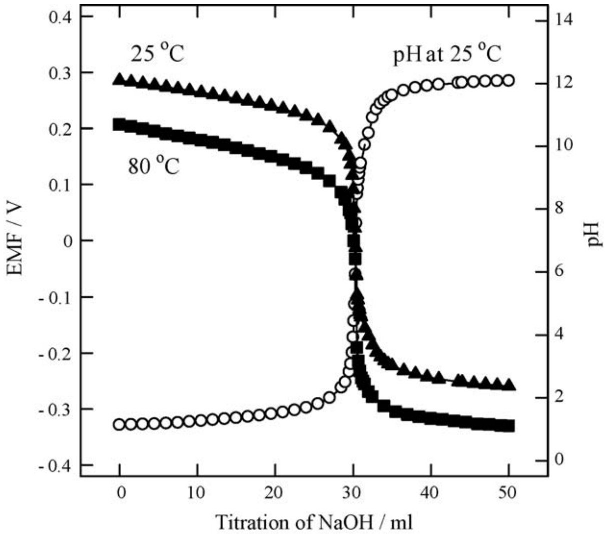

Fig. 6. Titration of 30 ml HCl aqueous solution with NaOH aqueous solution, with the all-solid-state pH sensor (▲, ■) and the commercial pH meter (○). The concentration of HCl aqueous solution: 0.1 mol/l. The concentration of NaOH aqueous solution: 0.1 mol/l.

measured.) The EMF of the all-solid-state pH sensor decreased linearly with an increase of temperature in any of the cases at pH 4.0 and pH 9.0. This result showed that the response was in accordance with the Nernst's equation. Accordingly, it was confirmed that this type of all-solid-state pH sensor showed good response characteristics even at high temperature (~80 °C) as well as the room temperature operation.

A normal pH titration test was performed by using 0.1 mol/l-NaOH and 0.1 mol/l-HCl solutions at 25 °C and 80 °C, and their results were shown in Fig. 6. The horizontal axis shows the dropped amount of 0.1 mol/l-NaOH solution, and the vertical axis shows the change of EMF of the all-solid-state pH sensor and the change of pH only at 25 °C. The pH titration curve shown in the figure was obtained by using a normal glass electrode. As for the all-solid-state pH sensor, good titration curves were obtained both at 25 °C and 80 °C. The equivalence point calculated from the curve at 25 °C obtained by using a commercial pH meter (Euttech instruments, Cyberscan pH 510) with a normal glass electrode was 29.75 ml. And, the equivalence point obtained from the measurement of EMF of this all-solid-state pH sensor was also 29.75 ml both at 25 °C and 80 °C. Those results were very similar to each other, and accordingly, it was confirmed that this type of all-solid-state pH sensor shows good response characteristics even at high temperature regions (~80 °C) as in the case of room temperature.

Although the absolute value of EMF of this sensor changed slightly as a result of using it to experiment for one year, the response characteristics described in this report were maintained.

4. Conclusion

All-solid-state pH sensor composed of solid-state indicator electrode and solid-state reference electrode was prepared to investigate the pH response characteristics from room temperature to 80 °C. The results can be concluded as follows:

1. All-solid-state pH sensor was successfully prepared by combining an Ag/AgCl reference electrode coated with Nafion film and an indicator electrode using $Li_5YSi_4O_{12}$ glass.
2. The EMF of the prepared all-solid-state pH sensor was almost independent of the presence of inorganic ions, and it works properly as a pH electrode in the pH range from 1.5 to 12.0.
3. This type of all-solid-state pH sensor shows good response characteristics in the temperature range from 20 °C to 80 °C, and it is promising for high temperature applications.

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