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Effect of heat-treatment on the pH sensitivity of stainless-steel electrodes as pH sensors

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Abstract

Effect of heat-treatment on the pH sensitivity of uncoated stainless-steel electrodes was investigated to comprehend the pH sensitivity of metal-oxide coated stainless-steel electrodes as novel pH sensors. The pH sensitivity of stainless-steel electrodes as-received and heat-treated at 500 °C, 600 °C and 700 °C for 24 h were 91 %, 94 %, 102 % and 91 %, respectively. The pH sensitivity tended to increase with increasing heat-treatment time at a given temperature. Thus, the most suitable heat-treatment condition for the stainless-steel electrodes was 600 °C for 24 h. The austenite phase (fcc) was the main phase on the surface of the heat-treated stainless-steel electrodes. Unexpectedly, the change in the martensite phase (bcc) as the second phase with heat-treatment temperature was similar to the pH sensitivity, with the martensite phase affecting the pH sensitivity. Therefore, it appeared that the pH sensitivity of the metal-oxide coated stainless-steel electrodes was affected by the underlying stainless-steel as well as the outer metal-oxide film coating. A prototype stainless-steel tube electrode was used as a working electrode for demonstrating the depth profiling of pH. The stainless-steel tube electrode showed good performance for measuring pH depth profiles compared to commercially available glass electrodes.

Keywords: Electrochemistry, Materials chemistry, Materials science

1. Introduction

Commercially available lithium silicate-based pH glass electrodes show ideal Nernstian pH sensitivity independent of redox interference, a short pH response time, high repeatability and a long lifetime, as well as high chemical durability over a wide pH range. However, the accumulated stain of the responsive glass membrane and liquid junction decrease pH sensitivity and increase pH response time.

For this reason, we have developed pH glass electrodes such as TiO₂-P₂O₅ glasses with a self-cleaning property based on photocatalytic activity and photoinduced hydrophilicity [1], and Fe₂O₃-Bi₂O₃-B₂O₃ glasses with an anti-fouling property based on their hydrophobicity [2, 3, 4].

The use of glass sensors is inappropriate for *in vivo* biomedical, clinical or food applications because of the brittleness of glass and the difficulty in measuring small volumes [5]. Therefore, low cost electrodes [6, 7, 8, 9, 10], solid state pH electrodes [11, 12, 13, 14, 15, 16] and disposable pH electrodes [6, 15, 17, 18, 19, 20, 21, 22, 23] have been developed. Stainless-steel is a strong candidate for a disposable metal pH electrode in terms of cost and suitable chemical durability. Although there has been a report of stainless-steel-based pH electrodes quite a while ago [17], it has not been followed up by subsequent studies.

Very recently, we reported that 3d-block metal-oxide coated stainless-steel electrodes heat-treated at 500 °C showed a pH sensitivity of 88–100 % [24]. Taking the pH response of Al and metal-oxide coated Al electrodes into consideration, it appeared that the pH sensitivity of the metal-oxide coated stainless-steel electrodes may be affected by the underlying materials as well as by the outer metal-oxide coated films. However, the effect of the heat-treatment condition (temperature and time) on the pH sensitivity of stainless-steel electrodes has not been clarified. In the present study, the relation between the pH sensitivity of stainless-steel (SUS304) heat-treated at different temperatures and the precipitated crystal phases was investigated.

2. Experimental

As a stainless-steel electrode, SUS304 (Nilaco Corporation, Tokyo, Japan) with a thickness of 0.1 mm was used. SUS304 was heat-treated at 500–700 °C for 24–96 h. For example, a sample name of SUS304-500-24 was used for SUS304 heat-treated at 500 °C for 24 h. The samples were directly put in furnace operating at a desired temperature and removed without furnace cooling after heat-treatment. All heat-treatment was carried out under air atmosphere. The notation OP was added for samples with an optically polished thermally oxidized layer outside the SUS304.

Potentiometric measurements were carried out for a handmade cell consisting of an SUS304 electrode with dimensions of 16 mm × 16 mm × 0.1 mm at 25 °C and time intervals of 3 s and 0.5 s using a pH meter F-73 (HORIBA, Ltd., Kyoto, Japan) and portable multi-logger ZR-RX20 (OMRON Corp., Kyoto, Japan), respectively. The details for the pH sensitivity are described in Refs. [1, 2, 3, 4, 24]. Potentiometric measurement of three cycles was run in order of pH 6.86 (150-7, monopotassium phosphate and disodium phosphate, HORIBA, Ltd., Kyoto, Japan, abbreviated as pH 7), pH 4.01 (150-4, potassium hydrogen phthalate, HORIBA, Ltd., Kyoto, Japan, abbreviated as pH 4) and pH 9.18 (150-9, sodium borate, HORIBA, Ltd., Kyoto, Japan, abbreviated as pH 9) according to JIS Z 8805. Potentials after 3 min in the third cycle at pH 7, pH 4 and pH 9 were read out as a stable one. In this case (25 °C), potential decreases ideally by 59.16 mV/pH with increasing pH according to Nernst equation.

The pH responsivity (pH sensitivity and pH response time) was determined as follows. Then, pH a–b sensitivity between pH a and pH b was estimated from potentials, E_a and E_b by the following Eq. (1),

$$\text{pH a – b sensitivity (\%)} = -100F(E_a - E_b)/2.3026RT(\text{pH a} - \text{pH b}) \quad (1)$$

where E_a , E_b , R , T and F are the potential of working electrode (prepared glass) versus reference electrode (Ag/AgCl) at pH_a and pH_b, the gas constant (8.3145 J/K mol), the absolute temperature and the Faraday constant (96485 C/mol), respectively.

The pH depth profile was measured using an SUS304-600-24 tube electrode (1.6 mm ϕ × pH response length 2 mm, with the rest of the part electrically insulated by covering with thermal shrinkage tube) and a commercially available pH glass electrode 9615S-10D (HORIBA, Ltd., Kyoto, Japan, 12 mm ϕ × pH response length ~13 mm). A pH 7 buffer solution with bromothymol blue (BTB) indicator was carefully placed on top of the pH 4 buffer solution with sugar to build a two-layer solution (upper pH 7 and lower pH 4). The pH electrode was immersed into the two-layer solution. The pH in the order of pH 7, pH 4, pH 7, pH 4 and pH 7 was measured by moving the electrode downward and upward at a rate of 0.1 mm/sec using dip coater F225S-Y (Asumi Giken, Ltd., Japan).

The crystalline phases precipitated in the heat-treated SUS304 were determined from XRD patterns measured using an Ultima IV instrument (Rigaku, Tokyo, Japan).

3. Results and discussion

The color of the heat-treated SUS304 was brown or deep blue due to the representative interference color compared with the silver color of the as-received SUS304, which results from the formation of the thermally oxidized layer outside the SUS304.

Fig. 1 shows the change in pH sensitivity of SUS304 electrodes heat-treated at a given temperature for varying heat-treatment times. The pH sensitivity of all the SUS 304 electrodes tended to increase with heat-treatment time at a given temperature. The pH sensitivity of SUS304-500-24 and SUS304-600-24 was 94 % and 102 %, respectively and was high compared to the as-received SUS304 (91 %) and SUS304-700-24 (91 %). The optimum heat-treatment temperature for the stainless-steel electrodes was 600 °C. However, the pH sensitivity of SUS304-600-24 decreased to 95 % after polishing the surface (not shown in Fig. 1). This indicates that the surface of SUS304-600-24 possesses high pH sensitivity compared to the underlying SUS304.

Fig. 2 shows the XRD patterns measured for the SUS304 electrodes as-received and heat-treated at 600 °C and 700 °C. The figure lying on the right-side is a view ranging from 40–55°. The figure lying on the left-side is a view enlarged to 30 times on the vertical axis ranging from 30–40°. It is seen from the figure on the right that diffraction lines are observed at approximately 43.5° and 51°, and 44.5°, which are assigned to austenite (JCPDS: No. 33-0397) and martensite (JCPDS: No. 35-1375) phases, respectively. The austenite phase increased with increasing heat-treatment temperature unlike the martensite phase. The small amount of thermally oxidized phases of Fe₂O₃ (JCPDS: No. 71-5088) and FeCr₂O₄ (JCPDS: No. 24-0511) are observed in the figure on the left. All peaks of most of the crystalline phases drastically decreased after surface polishing (SUS304-600-24-OP). This indicates that the outer layer has high crystallinity compared to the underlying SUS304. Since the outer layer has high pH sensitivity to the underlying SUS304, as mentioned above, we focused on the crystalline phases. The change in (a) pH sensitivity and (b) XRD peak intensity of SUS304 electrodes heat-treated at a given temperature for 24 h with heat-treatment temperature is shown in Fig. 3. The pH sensitivity showed a maximum at 600 °C, as seen on the left side of Fig. 3. It is seen from the right

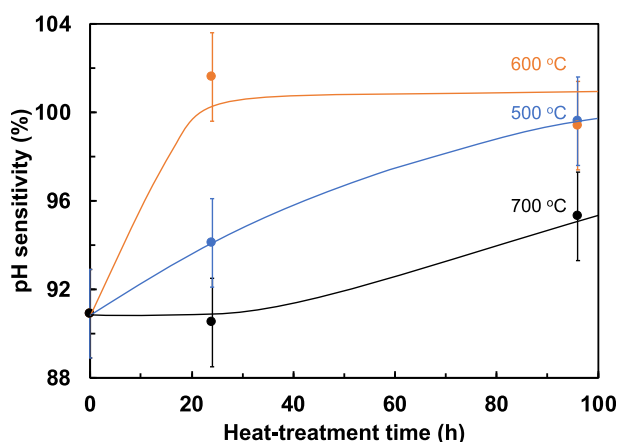


Fig. 1. Change in the pH sensitivity of SUS304 electrodes heat-treated at a given temperature with heat-treatment time.

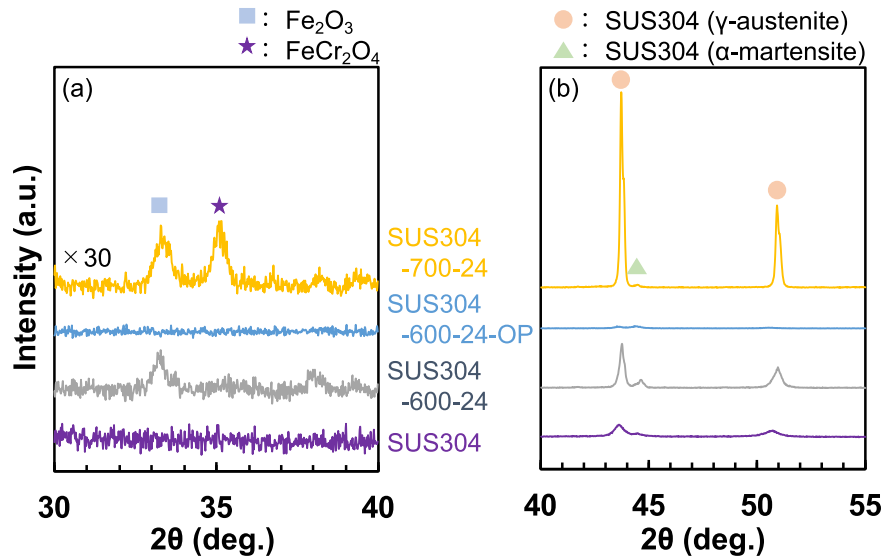


Fig. 2. XRD patterns of SUS304 electrodes as-received and heat-treated at 600 and 700 °C (a) $2\theta = 30\text{--}40^\circ$ (vertical axis is zoomed in thirty-fold) and (b) $2\theta = 40\text{--}55^\circ$.

side of Fig. 3 that the martensite phase changed irregularly whereas the austenite and Fe₂O₃ monotonically increased with increasing temperature. Thus, the change in pH sensitivity corresponded to that in the martensite of the second main phase. It is well-known that heat treatment of SUS304 increases martensite phase [25, 26, 27, 28]. Austenitic stainless steels suffer from sensitisation, when they are heat-treated

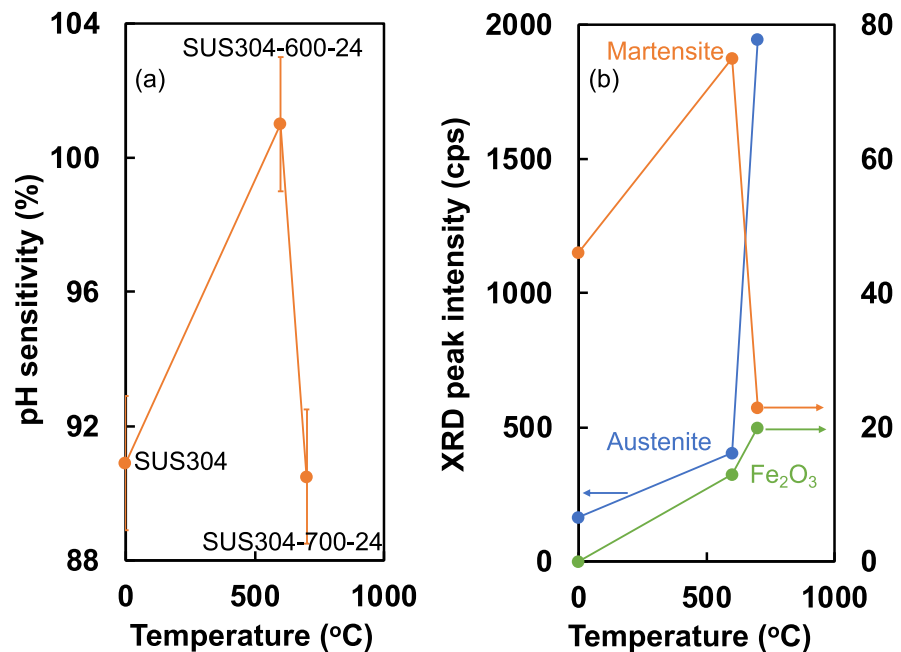


Fig. 3. Change in (a) pH sensitivity and (b) XRD peak intensity of SUS304 electrodes heat-treated at a given temperature for 24 h with heat-treatment temperature.

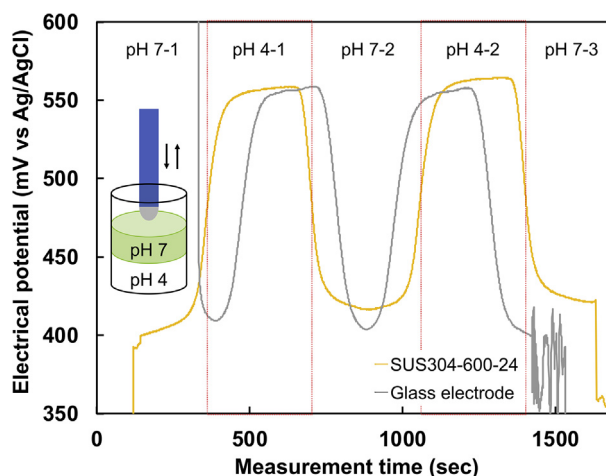


Fig. 4. Demonstration of pH depth profile measurement using an SUS304 tube electrode and commercially available pH glass electrode.

between 600 °C and 800 °C [28]. In a sensitised steel, the austenite near these boundaries and interfaces tends to transform to martensite phase. In addition, the martensite phase exists at surface compared to austenite phase [29]. This may result in the situation that martensite phase become more pH sensitive than austenite phase.

Both CuO/Al and Al electrodes showed an unstable and super-Nernstian potential in the same way, whereas CuO/SUS304 and SUS304 showed a stable and Nernstian potential, as reported previously [24]. This idea suggests that the pH sensitivity of metal-oxide coated Al electrodes is strongly affected by the underlying Al rather than by the outer metal-oxide film coating. In contrast, the effect of the surface of SUS304 on the pH sensitivity was observed in the present case. This result is because the SUS304 shows a Nernstian potential (pH sensitivity ~100 %) in contrast to the super-Nernstian potential (pH sensitivity ~200 %) of Al. Thus, the most prominent factor is the composition of the underlying materials and the second factor is the composition of the surface (oxidized layer and coated layer). If materials such as SUS304 with a pH sensitivity close to 100 % are used, the pH sensitivity of metal-oxide coated metal electrodes can be controlled by the composition of the surface. This corresponds to the case of 3d-block metal-oxide coated stainless-steel electrodes with a pH sensitivity of 88–100 % [24].

Thus, SUS304 electrodes heat-treated at 600 °C are favorable for obtaining working electrodes with high pH sensitivity. The measurement of pH depth profiles using an SUS304-600-24 tube electrode and commercially available pH glass electrode is demonstrated in Fig. 4 (Suppl. 1). The pH in the order of pH 7-1, pH 4-1, pH 7-2, pH 4-2 and pH 7-3 was measured. Since both electrodes are insufficiently immersed (partially in air) in the pH 7-1 and pH 7-3, the data obtained in pH 4-1, pH 7-2 and pH 4-2 will be discussed. The pH response curve of the glass electrode

was inconsistent with the pH profile of the solution, especially in the pH 7-2. On the other hand, the pH response curve of SUS304-600-24 tube electrode showed a quick response. This should be ascribed to the small size of the SUS304 tube electrode and the very short response time [24] compared to the glass electrode. Such metal electrodes are considered viable candidates for use as disposable pH electrodes, pH microelectrodes and tube and needle-type pH electrodes for novel pH sensors.

4. Conclusions

In the present study, the effect of heat-treatment on the pH sensitivity of uncoated stainless-steel electrodes was investigated to comprehend the pH sensitivity of metal-oxide coated stainless-steel electrodes as novel pH sensors.

The pH sensitivity of stainless-steel electrodes as-received and heat-treated at 500 °C, 600 °C and 700 °C for 24 h were 91 %, 94 %, 102 % and 91 %, respectively. The pH sensitivity tended to increase with increasing heat-treatment time at a given temperature.

The most suitable heat-treatment condition for the stainless-steel electrodes was 600 °C for 24 h. The austenite phase (fcc) was the main phase on the surface of heat-treated stainless-steel electrodes. Unexpectedly, the change in the martensite phase (bcc) as the second phase with heat-treatment temperature was similar to the pH sensitivity, with the martensite phase affecting the pH sensitivity. Therefore, it appeared that the pH sensitivity of the metal-oxide coated stainless-steel electrodes was affected by the underlying stainless-steel as well as the outer metal-oxide film coating.

A prototype stainless-steel tube electrode was used as a working electrode for demonstrating depth profiling of pH. The stainless-steel tube electrode showed good performance for measuring pH depth profiles compared to commercially available glass electrodes.

Declarations

Author contribution statement

Tadanori Hashimoto: Conceived and designed the experiments; Analyzed and interpreted the data; Wrote the paper.

Hiroki Kitabayashi, Kenta Ito: Performed the experiments.

Hiroyuki Nasu, Atsushi Ishihara: Analyzed and interpreted the data.

Yuji Nishio: Contributed reagents, materials, analysis tools or data.

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Competing interest statement

The authors declare no conflict of interest.

Additional information

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