Electrodeposited Cobalt-Iron Alloy Thin-Film for Potentiometric Hydrogen Phosphate-Ion Sensor

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ABSTRACT

A cobalt-iron alloy thin-film electrode-based electrochemical hydrogen-phosphate-ion sensor was prepared by electrodeposition on an Au-coated Al2O3 substrate from an aqueous solution of metal-salts. The use of a cobalt-iron alloy electrode greatly improved the hydrogen-ion sensor response performance, i.e., the sensor worked stably for more than 7 weeks and showed a quick response time of several seconds. Among the cobalt and iron alloy systems tested, the electrodeposited Co58Fe42 thin-film electrode showed the best EMF response characteristics, i.e., the sensor exhibited a linear potentiometric response to hydrogen-phosphate ion at the concentration range between 1.0 × 10⁻⁵ and 1.0 × 10⁻² M with the slope of –43 mV/decade at pH 5.0 and at 30°C. A sensing mechanism of the Co-based potentiometric hydrogen-phosphate ion sensor was proposed on the basis of results of instrumental analysis.

Keywords: Hydrogen-Phosphate Ion Sensor; Cobalt-Iron Alloy; Thin-Film Electrode; Electrodeposition

1. Introduction

Phosphate is an important element that is used widely for various industrial applications such as metal plating and food processing. However, phosphate has been a major factor of eutrophication in closed natural systems such as lakes, rivers and bays. Thus, determination of the exact amounts of (hydrogen)-phosphate ions in water systems has become important for environmental analysis. The conventional spectrophotometric method that is widely used has a high level of accuracy but is not suitable for on-site monitoring because of complex procedures including formation of a phosphate-molybdate complex. Considerable efforts have been made to develop high-performance ion sensors for monitoring hydrogen-phosphate-ion concentration, such as ion-selective electrodes [1-7], bio-related systems [8], hydroxyapatite-based electrodes [9], electrochromic devices [10,11], and amperometric devices [12,13]. Among these phosphate-ion sensors, ISE (ion-selective electrode)-based sensors using polymer membranes, with calixarene or molybdenum-acetylacetonate [14,15] are effective but still have problems in selectivity and/or stability. Xiao et al. reported that a cobalt metal electrode exhibited good potentiometric response and selectivity to dihydrogen-phosphate ion (H₂PO₄⁻) among common anions in an acidic medium [4]. Meruva and Meyerhoff showed that a Co-wire electrode responded well to hydrogen-phosphate (H₂PO₄⁻) and phosphate (PO₄³⁻) ions in different pH solutions [3]. It was revealed that a Co-wire-based hydrogen-phosphate ion sensor had a low concentration detection limit and a broad detection range [16-18]. A disposable on-chip hydrogen-phosphate ion sensor with planar cobalt micro-electrodes on a polymer substrate has also been reported [19]. These Co-based sensors are particularly attractive as hydrogen-phosphate ion sensors; however, a Co metal-based sensor seems to still lack stability for practical use. The sensing mechanism of the Co-based potentiometric sensor has still not been clarified.

In this study, it was found that the use of a cobalt-iron metal-alloy electrode drastically improved not only the stability of the sensor device but also its sensitivity to hydrogen-phosphate ion. A sensing mechanism of the Co-based potentiometric hydrogen-phosphate ion sensor was also proposed on the basis of characterization of the materials.

2. Experimental

A commercial alumina (Al₂O₃) sintered plate (SSA-T, 10 × 20 × 0.5 t: mm, Nikkato Ltd., Japan) was used as a substrate for the sensor devices. An Au coating (10 × 10 mm²) on Al₂O₃ as an electrode for electrodeposition was prepared by painting with Au-paste (TKK Ltd., Japan) and heating at 900°C. The prepared Au-attached alumina substrate and Pt plate (10 × 20 × 1 t: mm) were used as cathode and anode electrodes, respectively, for electrodepositing. The distance between the two electrodes was...
fixed at 10 mm.

The aqueous solution (250 mL) used for Co-only electrodeposition consisted of 1.1 mol/L CoSO₄·7H₂O, 0.022 mol/L H₃BO₃, and 0.051 mol/L NaCl with pH of 5.04. For Co-Fe alloy electrodeposition, metal sulfate solutions (A, B, and C) were firstly prepared as follows. Concentration ratios [CoSO₄·7H₂O] (mol/L)/[FeSO₄·7H₂O] (mol/L) in solutions A, B, and C were 0.090/0.270, 0.200/0.166, and 0.267/0.089, respectively. Metal sulfate solution (A, B, or C) consisting of 0.041 mol/L H₃BO₃ and 0.51 mol/L NaCl with pH of 2.00 and total volume of 250 mL was finally prepared for Co-Fe alloy electrodeposition. All metal thin-film electrodes were electrochemically deposited at a constant current of 100 mA/cm² for 180 s at room temperature.

The deposited metal films were characterized by means of X-ray diffractometry (XRD, JDX-3500K JEOL), X-ray photoelectron spectroscopy (XPS, JPS-90SX JEOL), and FT-IR spectroscopy (Magna760, Nicolet). Thicknesses of the metal-alloy electrodes were determined by scanning electron microscopy (FE-SEM, ERA8800, ELIONIX). Elemental composition of the prepared metal electrodes was determined by using an X-ray micro-analysis system (EDX, Genesis XM2 EDAX).

An electrochemical cell assembly (Metal electrode|sample solution||Ag/AgCl, KCl (sat.)) was used for potentiometric sensor measurements. Electromotive force (EMF) was measured by using an electrometer (R8240, Advantest Ltd.) in 0.1 M phthalate buffer solution with various anion concentrations between 1.0 × 10⁻⁶ and 1.0 × 10⁻² M at 30°C using their potassium salts.

3. Results and Discussion

3.1. Structure of the Metal Film Electrode

X-ray microanalysis of Co-Fe alloy electrodeposited films prepared from three different solutions (A, B, and C) revealed that the element compositions of Co and Fe in the alloys were at Co₃6Fe₆₄, Co₅₈Fe₄₂ and Co₇₅Fe₂₅, respectively, depending on the Co concentration in the electrolyte bath.

Figure 1 shows XRD patterns of the as-prepared Co and Co₅₈Fe₄₂ thin-film electrodes. Peaks observed in Figure 1(a) include an fcc phase of Co (JCPDS: #05-0727) and impurity phases of (β-)CoOOH (#14-0673) [20] and CoSO₄ (#11-125). They should be come from electrodeposition and the electrolyte solution used, respectively. As shown in Figure 1 (b), the Co₅₈Fe₄₂ metal alloy consists of a bcc phase of Co₅₈Fe₄₂ (#44-1433) as well as a trace amount of (γ-)FeOOH (#8-98). Other small peaks at 15 and 19 degrees (CuKα₁) are assigned to CoCl₂ (#15-381) and Co(OH)₂ (#30-443), respectively. Since most of the impurity phases easily dissolve in the aqueous solution during sensing, these metal thin-films mainly consist of metal-based electrodes.

Figure 2 shows SEM images of cross-sectional views of the Co and Co₅₈Fe₄₂ thin-film electrodes. They are adhered tightly onto the Au layer. The thicknesses of the Co and Co₅₈Fe₄₂ thin-film electrodes were about 0.8 and 1.0 μm, respectively.

3.2. Sensing Performance of the Metal Film Electrode

The Co metal thin-film electrode showed relatively good EMF response characteristic to H₃PO₄, as has already been reported by many researchers [4,16-19]. The prepared Co-only sensor responded well to H₃PO₄ in the concentration range of 1.0 × 10⁻⁴ to 1.0 × 10⁻² M, as shown in Figure 3(a). The 90% response time of the Co metal electrode to 1.0 mM H₃PO₄ was about 32 s.
was also found that the use of a Co-Fe alloy system electrode improved the response performance. As shown in Figure 3(b), the Co$_{58}$Fe$_{42}$ alloy thin-film electrode sensor responded more clearly to $\text{H}_2\text{PO}_4^-$ in the concentration range of $1.0 \times 10^{-4}$ to $1.0 \times 10^{-2}$ M, better than that of the Co-only electrode. The 90% response time of the Co$_{58}$Fe$_{42}$ alloy thin-film electrode to 1.0 mM $\text{H}_2\text{PO}_4^-$ was only 13 s. It was also found that the use of a Co-Fe alloy system electrode drastically improved the stability of the sensor. Although the Co-only thin-film electrode showed good EMF response to $\text{H}_2\text{PO}_4^-$ at the concentration range of $1.0 \times 10^{-4}$ to $1.0 \times 10^{-2}$ M, the response gradually shifted within 2 weeks as shown in Figure 4(a). On the other hand, it was revealed that the Co$_{58}$Fe$_{42}$ alloy thin-film electrode showed stable EMF response to $\text{H}_2\text{PO}_4^-$ in the concentration range of $1.0 \times 10^{-5}$ M to $1.0 \times 10^{-2}$ M for more than 7 weeks as shown in Figure 4(b).

Hydrogen-phosphate ion response characteristics of the Co-Fe thin film device, as a function of metal composition, are summarized in Table 1. It was shown out that the sensitivity and stability to $\text{H}_2\text{PO}_4^-$ depends on the composition of the electrode materials. The sensitivity here was expressed in terms of slope in the EMF change [mV/decade], as well as the 90% response time from 1 mM to 3 mM $\text{H}_2\text{PO}_4^-$.

In the Co-Fe system, the slope increased with increasing Fe content in Co-Fe alloy up to 42 at% Fe. Lower concentration limit was obtained using triple the background noise. Faster response time and long-term stability were also observed with increase in Fe content in the Co-Fe alloy up to 42 at% Fe. On the other hand, the sensor performances (slope, response time and stability) of the Co-Fe system decreased at higher Fe content of 64 at% Fe (Co$_{36}$Fe$_{64}$) in the Co-Fe alloy. Among the Co-Fe systems tested, the Co$_{58}$Fe$_{42}$ alloy thin-film electrode to $\text{H}_2\text{PO}_4^-$ in the concentration range of $1.0 \times 10^{-5}$ M to $1.0 \times 10^{-2}$ M for more than 7 weeks as shown in Figure 4(b).

### Table 1. Hydrogen-phosphate ion sensing characteristics of the Co-Fe thin-film device with various elemental ratios.

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<tr>
<td>Co</td>
<td>$1.0 \times 10^{-4}$</td>
<td>$-30$</td>
<td>32</td>
<td>3</td>
<td>Good</td>
</tr>
<tr>
<td>Co$<em>{25}$Fe$</em>{75}$</td>
<td>$1.0 \times 10^{-4}$</td>
<td>$-38$</td>
<td>30</td>
<td>4</td>
<td>Good</td>
</tr>
<tr>
<td>Co$<em>{42}$Fe$</em>{58}$</td>
<td>$1.0 \times 10^{-3}$</td>
<td>$-43$</td>
<td>13</td>
<td>7</td>
<td>Very good</td>
</tr>
<tr>
<td>Co$<em>{58}$Fe$</em>{42}$</td>
<td>$1.0 \times 10^{-3}$</td>
<td>$-16$</td>
<td>46</td>
<td>1</td>
<td>Poor</td>
</tr>
<tr>
<td>Fe</td>
<td>No response</td>
<td>-</td>
<td>-</td>
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<td>Poor</td>
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$^1$concentration range giving triple signal from the background noise; $^2$from 0.1 to 1.0 mM $\text{H}_2\text{PO}_4^-$. 

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**Figure 3.** EMF response transient of the Co$_{58}$Fe$_{42}$ thin-film electrode to hydrogen-phosphate ion at 30°C.

**Figure 4.** Stability of (a) Co and (b) Co$_{58}$Fe$_{42}$ thin-film sensors to hydrogen-phosphate ion at 30°C.
film electrode showed the best EMF response characteristic to $\text{H}_2\text{PO}_4^-$.

At this point, the sensing mechanism is a hypothesis. The tendency was similar for the magnetic relation for a Co/Fe alloy system [21]. This should be from the electric inter-molecule interaction between the Co/Fe electrode and the hydrogen-phosphate ion which has 3 electrons in a 3p orbital in the P-atom. This might be due to the high hydrogen-phosphate ion adsorption when Co/Fe alloys were introduced, and magnetic properties might therefore be important for the phosphate-ion sensing.

Phosphate-ion response characteristics of the Co$_{58}$Fe$_{42}$ thin-film electrode at various pH values are shown in Figure 5. Between pH 5.1 and 12.2, the best EMF response was observed at pH 5.1, indicating that this sensor easily responds to $\text{H}_2\text{PO}_4^-$ among the phosphate-based anions ($\text{PO}_4^{3-}, \text{H}_2\text{PO}_4^{2-}, \text{H}_3\text{PO}_4^-$). Figure 6 shows the selectivity of the Co$_{58}$Fe$_{42}$ thin-film electrode to various anions ($\text{HCO}_3^-, \text{NO}_3^-, \text{Cl}^-, \text{Br}^-, \text{CH}_3\text{COO}^-$ and SCN$^-$. Although EMF of the Co$_{58}$Fe$_{42}$ thin-film electrode responded to some anions within ±15 mV, this sensor showed excellent selectivity to $\text{H}_2\text{PO}_4^-$.  

### 3.3. Sensing Mechanism of the Co-Fe Metal Thin-Film Electrode

X-ray photoelectron (XPS) spectra [4,18,22] of the surfaces of the Co and Co$_{58}$Fe$_{42}$ thin-film electrodes before and after measurement to $\text{H}_2\text{PO}_4^-$ were investigated. Figure 7(a) shows Co 2p peaks of the Co-only thin-film electrode before and after measurements. Co$_{2p1/2}$ peaks appeared at 780.0 eV and 781.3 eV, and Co$_{2p3/2}$ peaks appeared at 796.4 eV and 797.1 eV, indicating that the surface of the Co thin-film was in both states of Co$^{2+}$ and Co$^{3+}$ before and after measurements. Figure 7(b) shows Co 2p peaks of the Co$_{58}$Fe$_{42}$ thin-film electrode before and after measurements, indicating that the Co$_{2p1/2}$ peaks for the surface of the Co$_{58}$Fe$_{42}$ thin-film existed in both states of Co$^{2+}$ and Co$^{3+}$ before and after measurements. It can also be seen that the Co$_{58}$Fe$_{42}$ thin-film electrode before the measurement included a richer state of Co$^{2+}$ than that of Co$^{3+}$. It is thought that Fe in the Co-Fe alloy reduces the state of Co from Co$^{3+}$ to Co$^{2+}$.
and then the Co$^{2+}$ state in the Co-Fe alloy was more stabilized than that in the Co-only electrode. It was also revealed that the state of Co$^{3+}$ after sensor measurements was richer than that of Co$^{2+}$ in the Co$_{58}$Fe$_{42}$ thin-film, although they also showed both Co$^{2+}$ and Co$^{3+}$ states. 

Figure 8 shows Fe 2p peaks of the Co$_{58}$Fe$_{42}$ electrode before and after measurements. Fe$_{2p3/2}$ peaks before the measurement appeared at 709.4 eV and 711.4 eV, indicating the presence of both states of Fe$^{2+}$ and Fe$^{3+}$ on the surface of the film. After the sensor measurement, the peak at 709 eV decreased and insisted on the peak at 711.6 eV of Fe$^{3+}$. Thus, it turned out that the surface of the Co$_{58}$Fe$_{42}$ thin-film electrode was in the state of coexistence of Fe$^{2+}$ and Fe$^{3+}$ before the measurement, and it changed to a richer state of Fe$^{3+}$ than that of Fe$^{2+}$ after exposure to the electrolyte.

FT-IR spectra of the Co$_{58}$Fe$_{42}$ thin-film electrode before and after measurements for hydrogen-phosphate ion sensing are shown in Figure 9. Absorptions of ν(Co-O) and ν(Fe-O) at around 484 and 791 cm$^{-1}$, respectively, appeared before the measurement [23,24]. Absorptions at around 1030, 1100 and 1600 cm$^{-1}$ should be indicated for ν(BO$_3^{2-}$), ν(SO$_4^{2-}$) and ν(OH$^-$) from the electrolyte, respectively. Large absorption at 1360 cm$^{-1}$ for ν(MOOH) should be come from FeOOH, as also observed in Figure 1.

After the sensor measurement, broad absorptions of ν(Co-O) appeared at around 482 and 553 cm$^{-1}$. Absorption of ν(Fe-O) also appeared at 752 and 810 cm$^{-1}$. The M-O (M = Co, Fe) band shifted to a higher wave number, indicating that lower-valence metal ions (Co$^{2+}$, Fe$^{2+}$) are oxidized to higher-valence metal ions (Co$^{3+}$, Fe$^{3+}$), as also shown by the XPS results.

Moreover, absorption of ν(H$_3$PO$_4^-$) newly appeared at 1040 cm$^{-1}$ [24]. The Co-site seems to be more sensitive to hydrogen-phosphate ion than that of Fe in the Co-Fe alloy, and the sensitivity to H$_3$PO$_4^-$ was thus decreased at the highest Fe content in the Co-Fe alloy, as shown in Table 1. When the XPS and FT-IR spectra were taken into consideration, the surface of the Co-Fe electrode before measurement formed Co$_3$O$_4$ (Co(II), Co(III)) and Fe$^2$O$_4$(Fe(II), Fe(III)) and changed after measurement to Co(H$_3$PO$_4$)$_3$ (Co(III)) and Fe(H$_3$PO$_4$)$_3$ (Fe(III)) (or FeOOH), respectively.

The slope of the line for EMF versus log[H$_3$PO$_4^-$] was largely dependent on the electrode materials. Thus, the sensing mechanism seems arise not from the conventional Nernst’ type but probably the mixed potential one, as already reported [3,18]. When the sensing electrode is exposed to H$_3$PO$_4^-$ ion including dissolved oxygen, electrochemical reduction (1) and electrochemical H$_2$PO$_4^-$ oxidation (2), (2’) take place simultaneously.

\[
\begin{align*}
\text{O}_2 + 4\text{H}^+ + 4e^- & \rightarrow 2\text{H}_2\text{O} \quad (1) \\
\text{Co}_3\text{O}_4 + 9\text{H}_2\text{PO}_4^- + 8\text{H}^+ & \rightarrow 3\text{Co} (\text{H}_3\text{PO}_4)_3 + 4\text{H}_2\text{O} + e^- \quad (2) \\
\text{CoO} + 3\text{H}_2\text{PO}_4^- + 2\text{H}^+ & \rightarrow \text{Co} (\text{H}_3\text{PO}_4)_3 + \text{H}_2\text{O} + e^- \quad (2')
\end{align*}
\]

The two cathodic and anodic electrochemical reactions form a local cell and determine the mixed electrode potential. Figure 10 shows schematic polarization curves for both the anodic and cathodic reactions. As a sensor device, the sensing signal of the Co-Fe electrode should be a more accurate value than the Co-only one, that is, the slope of EMF versus log[H$_3$PO$_4^-$] should be larger. When we consider cases (C-I) and (C-II) for cathodic reaction as shown in Figure 10, the mixed potentials gave a larger slope in the order of (C-I) > (C-II). The value of the slope $E$ versus log I at the small current area

**Figure 8.** XPS spectra of iron on the surface of the Co$_{58}$Fe$_{42}$ thin-film electrode before and after measurements for hydrogen-phosphate ion sensing.

**Figure 9.** FT-IR spectra of the Co$_{58}$Fe$_{42}$ thin-film electrode before and after measurements for hydrogen-phosphate ion sensing.
mixed potential mechanism of the Co-based potentiometric sensor were proposed from XRD, XPS and FT-IR measurements. Further development of materials of the metal-alloy system should improve the sensor performance.

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REFERENCES


