



# Phosphate ion sensor using a cobalt phosphate coated cobalt electrode

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## ABSTRACT

Phosphorous is one of three major nutritional elements for plants and usually exists as phosphate ions in nature. For hydroponic culturing and wastewater treatment, the development of a high-performance phosphate sensor would be very helpful. A novel phosphate ion-selective electrode was constructed using a cobalt phosphate surface coated cobalt electrode. The potential response seems to be caused by the formation of  $\text{Co}(\text{H}_2\text{PO}_4)_2$  in the coexistence of  $\text{CoO}$  and  $\text{Co}(\text{OH})_2$ . The sensor exhibited a linear response to  $\text{H}_2\text{PO}_4^-$  in the concentration range from  $1.0 \times 10^{-5}$  to  $1.0 \times 10^{-1} \text{ mol L}^{-1}$  at a pH range from 4.0 to 6.5 with a slope of  $-39 \text{ mV dec}^{-1}$ . The sensor was unaffected by common anions, such as chloride, carbonate, and sulfate. The electrode maintained stability for at least 4 weeks in a live hydroponics system when sufficient  $\text{Co}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$  was deposited on the Co electrode.

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## 1. Introduction

Phosphate ion analysis has become a hot topic in recent decades for advanced hydroponic culturing and environmental wastewater treatment [1,2]. The concentration of phosphate ion is usually determined using high-performance liquid chromatography or spectroscopic methods using the molybdenum blue reaction, complex formation of molybdophosphate with basic dye compounds, and indirect determination with lanthanum chloranilate after a sample pretreatment, such as filtration and solution preparation [3–6]. Thus, it is difficult to continuously monitor the concentration of phosphate ions. In recent decades, electrochemical measurements using ion-selective electrodes (ISE) have been developed. ISE allow for simple, fast, stable, low cost, and portable analysis of target analytes [7–17]. For phosphate ISEs, various approaches have been attempted: 1) metal/metal compound coupling electrodes [7–12]; 2) solid membrane electrodes [13]; 3) heterogeneous metal membrane electrodes [14]; and 4) polyvinylchloride (PVC) membrane electrodes impregnated with organic solutions [15–17]. In particular, cobalt has often been utilized as a base material for the phosphate sensor [2,12,18–25]. Xiao et al. reported that the cobalt electrode, the surface of which was coated by a cobalt oxide (CoO) layer, showed a selective potentiometric response to  $\text{H}_2\text{PO}_4^-$  and the reporting mechanism of the

CoO-modified electrode was discussed based on the host-guest chemistry of a nonstoichiometric cobalt oxide compound [7]. Meruva and Meyerhoff proposed a mixed potential mechanism based off the behavior of the Co electrode in the presence of phosphate and oxide species [18]. Although many studies exist on the types of phosphate-sensing Co electrodes, including a micro-electrode type [19–21], a cobalt film type [22,23], a screen printing type [24], and a flow injection type [2,25], the proposed mechanism by Meruva and Meyerhoff appears to be universally applicable. On the other hand, Kidosaki et al. suggested a different response mechanism [26]. They believed that the reporter compound was  $\text{Co}(\text{H}_2\text{PO}_4)_2$  and that the reaction was coupled with the reduction of oxygen. Since it is well known that the potential of the Co-modified electrode is not stable, the details of the reporting mechanism are still unclear [8,10]. In addition, the influence of pH in the monitoring system on the stability of the Co-modified electrode has been reported [19]. In the present study, an ISE for the dihydrogenphosphate ion ( $\text{H}_2\text{PO}_4^-$ ) was constructed by electrodepositing cobalt phosphate hydrate ( $\text{Co}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ ) onto the surface of the Co electrode. The electrochemical characteristics were then evaluated and the  $\text{H}_2\text{PO}_4^-$  reporting mechanism was investigated by considering a mixed potential system.

## 2. Experimental

### 2.1. Reagents

All chemical reagents were of analytical grade and were used

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without further purification. Co wire ( $\phi$ 1 mm, 99.99%) was purchased from the Nilaco Co., Ltd. Sodium dihydrogenphosphate dihydrate ( $\text{NaH}_2\text{PO}_4$ ), sodium hydrogenphosphate monohydrate ( $\text{Na}_2\text{HPO}_4$ ), potassium nitrate ( $\text{KNO}_3$ ), sodium chloride ( $\text{NaCl}$ ), sodium sulfate ( $\text{Na}_2\text{SO}_4$ ), sodium acetate ( $\text{CH}_3\text{COONa}$ ), sodium hydrogencarbonate ( $\text{NaHCO}_3$ ) and sodium hydroxide ( $\text{NaOH}$ ) were purchased from Wako. Co. Ltd. Hydrochloric acid ( $\text{HCl}$ ) was obtained from Kishida Co. Ltd.

## 2.2. Apparatus

Electrochemical measurements were conducted using electrometers HE-106A (Hokuto Denko Co., Ltd.), a potentiostat/galvanostat HA1010mM1A (Hokuto Denko Co., Ltd.), a function generator HB305 (Hokuto Denko Co., Ltd.) and an A/D converter (GL900, Graphtec. Co., Ltd. The electrode surface before and after the electrolysis was observed by a scanning electron microscopy VHX-D500 (Keyence Co., Ltd.). By use of pH meter PH-230SD (Lutron Co., Ltd. Taiwan), the pH of the solution was prepared and measured. The concentration of dissolved oxygen, DO, in the aqueous solution was measured by an oxygen electrode E101 (Optoscience Co., Ltd.). According to the methods of Lee et al. [19], argon, air and oxygen were bubbled for several minutes until the current of an oxygen sensor was kept at a constant value in order to prepare 0%, 21% and 100% DO solutions. The saturated concentration of  $\text{O}_2$  in water (at 20 °C) is estimated at about 8.75 mg  $\text{L}^{-1}$ , and the potentiometric response is similar to that in the case of about 21%. Here, the concentration of oxygen in the test solution was monitored with a commercial oxygen electrode. The chemical composition of the electrodeposits was examined by an XRD meter SmartLab (Rigaku Corp.).

## 2.3. Preparation of Co modified electrodes

At first, the surface of the cobalt wire (diameter:  $\phi$ 1 mm, length: 100 mm) was polished by sandpapers of #80, #240 and #1000, respectively. It was then washed for 30 min by an ultrasonic cleaner. The cobalt wire was covered with a silicone tube except both ends of the electrode, and one end of the silicone tube was coated with epoxy resin to avoid the penetration of the solution into the gap between the cobalt electrode and the silicone tube. Thus one end of the cobalt wire of which length was 10 mm was used as a working electrode. The electrode was used for the measurement of cyclic voltammograms.

In order to coat the electrode surface with the cobalt phosphate, the constant potential ( $-0.3$  V vs.  $\text{Ag}|\text{AgCl}|\text{sat. KCl}$ ) was applied for about 2 h until the anodic current decreased to about 0 A, as shown in the inset of Fig. 2. After the surface of the Co electrode was washed with double distilled water, the modified electrode was dried and was stored in Argon gas atmosphere.

## 2.4. Electrochemical measurement

All potentiometric measurements were carried out with a two-electrode system using a saturated  $\text{Ag}|\text{AgCl}$  reference electrode and phosphate-sensing electrodes (3 sets as parallel), and both a temperature and an oxygen sensors were used simultaneously. In the present study, the ISE potential was measured under constant DO concentrations (about 8.75 mg  $\text{L}^{-1}$ ) by bubbling air through the system except when DO concentration was changed.

## 3. Results and discussion

### 3.1. Cyclic voltammograms of Co electrode in phosphate ion system

Cyclic voltammograms were obtained using the Co electrode in aqueous solutions in the presence and absence of  $\text{NaH}_2\text{PO}_4$  at pH 7, as shown in Fig. 1. The potential was scanned for four cycles in the range from  $-1.2$  V to 0 V (vs.  $\text{Ag}|\text{AgCl}|\text{sat. KCl}$ ) at a scan rate of 50  $\text{mV s}^{-1}$ . In the absence of  $\text{H}_2\text{PO}_4^-$ , the anodic current started to flow at  $-0.35$  V and two cathodic peaks appeared at  $-0.74$  V and  $-0.82$  V, respectively, in the negative potential scan. Based on the Pourbaix diagram in Fig. S1, the standard potential of the  $\text{Co}|\text{Co}^{2+}$  couple is around  $-0.48$  V [27]. Thus, the two cathodic peaks can be assigned to the reduction of  $\text{Co}^{2+}$  to Co, caused by the reduction of  $\text{Co}(\text{OH})_2$  and/or Co oxides ( $\text{CoO}$  and/or  $\text{Co}_2\text{O}_3$ ), respectively. By considering the pH value of the experiment, the reduction of  $\text{Co}(\text{OH})_2$  was more probable than that of Co oxides. In the presence of  $\text{H}_2\text{PO}_4^-$  under aqueous conditions (curve b), another anodic peak appeared around  $-0.3$  V, and the anodic wave that existed at the more positive potential (like the final rise) in the absence of  $\text{H}_2\text{PO}_4^-$  disappeared. The anodic peak seems to appear due to the formation of cobalt phosphate since the anodic peak height was  $\text{H}_2\text{PO}_4^-$  concentration dependent, as expressed from Fig. S2. In this case, the following reactions are believed to occur on the surface of the Co electrode in this potential region.



In addition, the anodic current peak height greatly decreased when the pH approached the  $\text{pK}_{\text{a}2}$  value (7.2) of phosphate and the potential scanning rate increased, as expressed in Figs. S3 and S4. Taking into account these characteristics, that  $\text{Co}(\text{H}_2\text{PO}_4)_2$  is the response active material to  $\text{H}_2\text{PO}_4^-$  under aqueous conditions is predictable [28]. Accordingly, the Co electrode coated by cobalt phosphate on the surface was fabricated as a  $\text{H}_2\text{PO}_4^-$ -ISE electrode. The anodic current, due to the oxidation of Co, which appears above  $-0.35$  V was inhibited by the cobalt phosphate layer. There are two cathodic peaks in curve b of Fig. 1. The peak appearing near  $-0.82$  V is the same cathodic peak observed in the absence of  $\text{H}_2\text{PO}_4^-$  (curve a of Fig. 1), and the cathodic wave is thought to result from the reduction of  $\text{Co}(\text{OH})_2$  (and/or  $\text{CoO}$ ) to Co. The other peak appearing near  $-1.04$  V was attributed to the reduction of  $\text{Co}(\text{H}_2\text{PO}_4)_2$  to Co. Fig. 2 presents the cyclic voltammograms of the

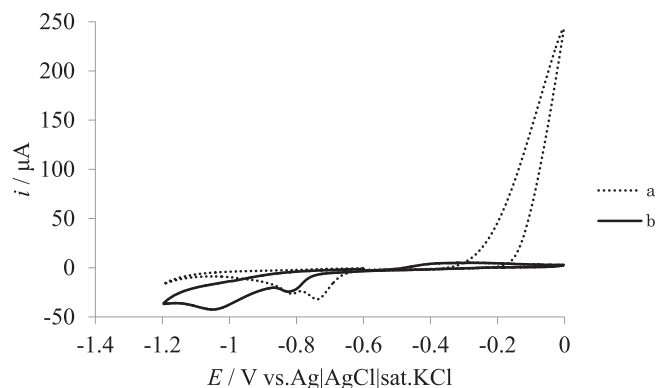


Fig. 1. Cyclic voltammograms of the cobalt electrode in 0.1 M  $\text{NaCl}$  (a) and 0.1 M  $\text{NaH}_2\text{PO}_4$  (b) at pH 7. Potential scanning rate: 50  $\text{mV s}^{-1}$ . Electrode area: 0.785  $\text{mm}^2$ .

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