

Study of Cobalt Nanoparticle Modified Gold Electrode

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Phosphate detection using Cobalt nanoparticle modified gold electrode has been carried out. Cobalt oxide nanoparticles were produced by mixing a solution of cobalt chloride with 10 % glycerol and adding Ammonium hydroxide solution with stirring for 2 hours at 50 °C using a magnetic stirrer. The solution was then allowed to stand for 12 hours. The precipitate obtained was filtered and calcined at 700 °C for one hour. The obtained cobalt nanoparticles are mixed with nafion, then attached to a gold wire to form a modified cobalt nanoparticle electrode. The performance of this electrode was tested against a phosphate solution using a three-electrode system of the Autolab Metrohm type AUT 84948. Measurements were made by immersing a modified cobalt gold electrode connected to the Metrohm Autolab three-electrode system. All phosphate measurements were carried out in KHP and KCl buffer solutions. Voltammograms of KHP did not show peaks of anodic and cathodic currents but in phosphate solution (10 ppm NaH_2PO_4) showed peaks of cathodic currents at a potential of -1.009 V. This indicated that the electrode was sensitive to phosphate ion solutions. The cathodic current increases with the phosphate concentration. The measurement detection limit is 0.47 ppm.

Keywords: Cobalt electrode, Phosphates, Potentiometry, Cyclic voltammetry, Sensor.

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1. INTRODUCTION

Phosphates have attracted the attention of researchers recently. We can find phosphate almost everywhere because it is known as a water pollutant. Excessive amounts of phosphate can cause eutrophication of water and its surroundings because phosphate in water is a source of life for phytoplankton [1, 2]. The increasing population of phytoplankton eventually affects the proliferation of algae and other plankton, causing the dissolved oxygen content in the water to greatly decrease [3, 4]. Therefore, the phosphate content in the water must be monitored. The standard method commonly used to detect phosphate is the colorimetric method because this method is quite accurate, has good resolution, and has a low detection limit (20-150 nM) [5, 6]. However, this method has several drawbacks including the need for toxic chemicals which are generally expensive, it has relatively complicated procedures, requires trained personnel, and a heavy workload when applied in large samples. This commercial colorimetric method requires compensation and correction because the turbidity level of the sample directly affects the measured absorbance value and also the number of other disturbances. Thus, methods and equipment are needed that can be simple, fast, and real-time to be able to monitor the phosphate content in water.

Recently, researchers start to develop electrochemical phosphate ion sensors for environmental analysis due to their high selectivity and sensitivity, wide linear range, and fast response time. Amperometric and potentiometric sensors are electrochemical phosphate ion sensors that have been developed. Amperometric sensors usually have a relatively low limit of detection but monitoring in situ is long-term because the rotation of

the electrodes requires quite high energy. Current-based (amperometric) sensors that can detect phosphate in the submicromolar range require enzymes that can cause stability problems in environmental conditions [6]. Meanwhile, potentiometric sensors have a slightly better linear range than amperometric sensors [7-9]. Potentiometric sensors are widely used because their detection is quite fast, the instrument is simple and the manufacturing process is easy. Among potentiometric sensors, cobalt electrodes are very popular because they have several advantages such as no additional reagents, fast detection and easy miniaturization. However, these cobalt-based sensors are limited by their high detection range ($> 10^{-6}$ M) [4], [10]. In this research, we will make a cobalt nanoparticle-based electrode that can show fast response and much better sensitivity with very easy and simple fabrication.

2. DESCRIPTION OF OBJECTS AND INVESTIGATION METHODS

2.1 Tools

The equipment used in this study includes an Autolab Metrohm type AUT84948 three-electrode system, beaker, measuring pipette, Ohaus analytical balance, spatula, glass bottle, 25 mL volumetric flask, Oakton pH meter, Thermo Scientific oven, heater (hot plate)

2.2 Material

All reagents are of analytical grade and are used without further purification. Au wire (ϕ 1 mm, 99.99%) was purchased from PT. Antam, Tbk, cobalt (II) chloride ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$), sodium dihydrogen phosphate ($\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$), potassium hydrogen phthalate, hy-

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drochloric acid, potassium chloride (KCl), Ammonia solution (NH₄OH), hydrochloric acid (HCl), and Kalium hydrogen phthalate (KHP) and Nafion™ were purchased from Merck & Co.

2.3 Procedure

2.3.1 Preparation of Cobalt Nanoparticle

Cobalt nanoparticles were prepared by mixing 0.1 M CoCl₂·6H₂O solution with 10 % glycerin to 500 mL. This solution mixture was then stirred using a hotplate stirrer and 0.1 M 50 mL NH₄OH solution was added little by little at 50 °C for 2 hours. The mixed solution was then allowed to stand for 12 hours. Filter the precipitate using oven filter paper at 50 °C for 2 hours. The precipitate that has been oven is then separated from the filter paper and in the furnace for 1 hour at 700 °C

2.3.2 Preparation of Co Modified Electrodes

The preparation of a modified cobalt gold electrode is by mixing the cobalt nanoparticles with Nafion on a glass cup and then coating it on the prepared gold electrode using a 1 cm long brush. The gold electrode that has been coated with cobalt is then inserted into the shrinkage cable.

2.3.3 Preparation of Co Modified Electrodes

Measurement of the sensor's electrical response and potential difference between the working electrode (cobalt-modified gold) and the reference electrode (Ag/AgCl) used the Autolab Metrohm type AUT84948 three-electrode system. Tests Measurement of electrode response was carried out by measuring standard phosphate with a concentration range of 1 to 10 ppm. All measurements were carried out by dipping a modified cobalt gold electrode connected to the Autolab Metrohm type AUT84948 three-electrode system.

3. RESULTS AND DISCUSSION

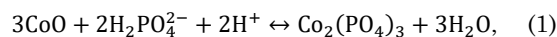
3.1 Electrochemical Characteristic of Co Modified in Buffer and NaH₂PO₄ Solution

Analysis To determine the reaction potential of the cobalt electrode with phosphate ions, a cyclic voltammogram curve was used to analyze it. As shown in Fig. 1, the cobalt electrode has a cathodic peak of around -1.004 V in Potassium hydrogen phthalate at pH 4 and a fairly clear cathodic peak at -1.009 V in sodium dihydrogen phosphate solution at pH 4. Comparing the two curves proves that the peak The -1.009 V may be related to the reaction of the phosphate ion.

3.2 Electrochemical Characteristic of Co in Various Concentrations of NaH₂PO₄

Analysis To determine the properties of the cathodic peaks, we tested the concentration dependence of the cobalt electrode in different phosphate solutions. As shown in Fig. 2, when the concentration of sodium dihydrogen phosphate increased from 1 ppm to 8 ppm,

the peak negative cyclic voltammogram also increased. Because phosphoric acid contains polybasic acids, phosphoric acid has three stages of dissociation in an aqueous solution, namely dihydrogen phosphate, mono hydrogen phosphate, and phosphate. The pH of the solution greatly affects the fraction of each form. At pH 4, the most dominant phosphate is dihydrogen phosphate:



The conversion of cobalt oxide to cobalt phosphate upsets the existing equilibrium because the conversion consumes the cobalt oxide. A more stable condition can be formed by further oxidation of the cobalt electrode with a negatively shifted potential [10].

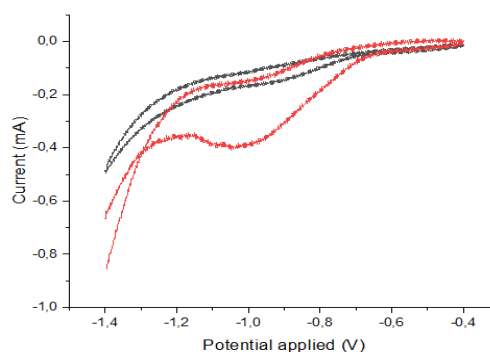


Fig. 1 – Cyclic Voltammogram of cobalt electrode in KHP and KCl (a) and 10 ppm NaH₂PO₄ at pH 4

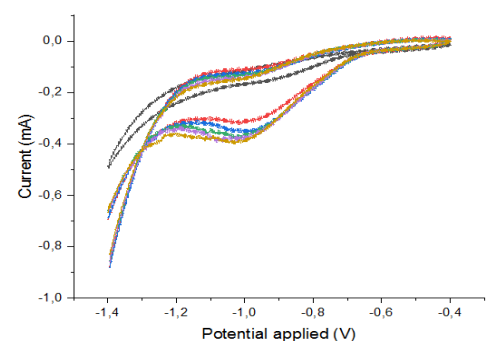


Fig. 2 – Cyclic Voltammogram in various concentrations of NaH₂PO₄ at pH 4; 0 ppm (black), 1 ppm (red), 2 ppm (blue), 4 ppm (green), 6 ppm (purple), and 8 ppm (brown).

3.3 Calibration Curve

Fig. 3 shows the calibration curve for phosphate ions with a concentration of 1 ppm to 8 ppm NaH₂PO₄ calculated from cyclic voltammogram calculation data. The curve shows a linear relationship in the dynamic range with a slope of -11.08. The dynamic range in this study is at least better than previously reported studies from 10⁻⁵ to 10⁻² M [11-14]. All our electrochemical experiments were carried out at 50 mV/s because the cyclic voltammogram curve is stable at scan rate. this with a good reduction peak of about -1.009 V. The detection limit of the cobalt electrode is estimated to be 0.47 ppm using the relation 3σ_b, where σ_b is the standard deviation of the non-phosphate buffer solution. To determine the standard deviation, experiments were carried out at each concentration at

least three times. The magnitude of the sample peak current response is used to plot the calibration curve. The R-square coefficient of the linear fit is 0.9353. It can be seen that the cathodic peak is formed due to the reaction between the cobalt electrode and the phosphate ion [9].

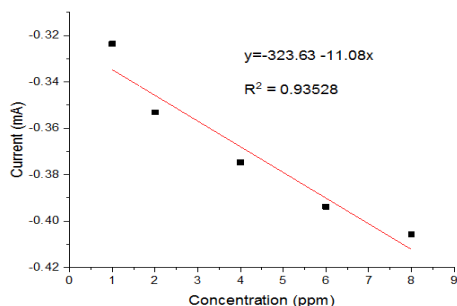


Fig. 3 – Concentration dependence of the cathodic peak

3.4 Comparisons of the Sensors Prepared in This Study with Existing Methods

Table 1 – The results reported in the literature using several methods for detecting phosphates.

Method	Limit of Detection	Ref
Spectrophotometri	5×10^{-1} mg/L	[15]
Fluometric	5×10^{-1} μ M	[16]
Colorimetric	5×10^{-1} μ M	[17]
Molybdenum based sensor	1.9×10^{-6} M	[18]
Colorimetric	13×10^{-1} and 28×10^{-1} ppm	[19]
This study	4.7×10^{-1} ppm	

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Дослідження електрода із золота, модифікованого наночастинками кобальту

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Було проведено виявлення фосфатів за допомогою золотого електрода, модифікованого наночастинками кобальту. Наночастинки оксиду кобальту отримували змішуванням розчину хлориду кобальту з 10 % гліцерином і додаванням розчину гідроксиду амонію при перемішуванні протягом 2 годин при 50 °C. Потім розчин залишали на 12 годин. Отриманий осад відфільтрували і відпалили при 700

°C протягом години. Отримані наночастинки кобальту змішали з нафіоном, потім прикріпили до золотого дроту для формування модифікованого електрода з наночастинок кобальту. Ефективність цього електрода перевіряли у порівнянні з розчином фосфату за допомогою триелектродної системи Autolab Metrohm типу AUT 84948. Вимірювання проводили шляхом занурення модифікованого кобальтового золотого електрода, підключеного до триелектродної системи Metrohm Autolab. Усі вимірювання фосфатів проводили в буферних розчинах KHP і KCl. Вольт-амперограми KHP не показали піків анодного та катодного струмів, але у фосфатному розчині (10 ppm NaH_2PO_4) показали піки катодних струмів при потенціалі $-1,009$ В. Це вказувало на чутливість електрода до розчинів фосфатних іонів. Катодний струм зростає зі збільшенням концентрації фосфату. Межа виявлення вимірювання становить $0,47$ ppm.

Ключові слова: Кобальтовий електрод, Фосфати, Потенціометрія, Циклічна вольт-амперометрія, Сенсор.