# Electrodeposition of Cobalt on the Carbon Surface from Cobalt Sulfate Solution by Cyclic and Linear Voltammetry in Developing Selective Electrodes for Phosphate Ion

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**Abstract.** Phosphorus in nature is very important both in water and in soil. The form of the compound phosphate has become an important study in agriculture and the environment. Potentiometry is a recommended effective method to measure or monitor ion phosphate's concentration in nature compared to the spectrometric method, as supporting information for further purposes. However, the problem is the unavailability of suitable sensors or those are rarely found. Thus, this study reports the development of electrodes made from cobalt as an active part in the potentiometric detection of phosphate ions. Cobalt was immobilized electrochemically on the surface of carbon rods using cyclic (CV) and linear sweep (LSV) voltammetry methods in a potential range from 0 mV to $-1000$ mV. The amount of cobalt deposited was measured spectrometrically, and the morphology of the cobalt-carbon electrode is captured by SEM. The amount of electrodeposited cobalt was higher in LSV-based electrodes than in CV-based electrodes. Consequently, the electrode performance tested by the potentiometry method showed that LSV-based has better performance (linear region, sensitivity, and reproducibility) than CV-based electrodes.

**Keywords:** Cobalt Electrodeposition · Voltametry · Potentiometry · Selective Electrode · Phosphate Ion

## 1 Introduction

Phosphorus (P) is one of the essential macro soil elements that plants need in large amounts, in addition to nitrogen (N) and potassium (K) [1]. Phosphorus in nature combines with oxygen to form phosphate compounds, and plants absorb phosphorus in the form of inorganic phosphate ions such as $H_2PO_4^-$ and $HPO_4^{2-}$. The availability of phosphorus is essential for plant growth, but its presence in an uncontrolled environment is hazardous, so it is necessary to monitor phosphorus regularly. Monitoring activities regularly require measuring tools that are simple, practical, energy-efficient, and mobile.

In a review, Kim and co-workers stated that phosphate sensors, one of the important components in a measuring instrument, can be classified into three types, namely polymer

membrane type, protein biosensor type, and cobalt type electrode [2]. Studies on the performance of sensors based on ion-selective membranes and cobalt-based electrodes for phosphate measurements have proven that cobalt-based electrodes have a better response in the working area of from $10^{-5}$ mol/L to $10^{-1}$ mol/L compared to phosphate ion-selective membranes which only cover the range concentration from $10^{-4}$ mol/L to $10^{-1}$ mol/L [3].

So far, it is known that there is no cobalt-based phosphate sensor on the market, so research on this still needs to be done. Several researchers make cobalt-based phosphate sensors through the electrodeposition process of cobalt on metals or other substrates such as gold [4], copper [5], and carbon [6]. Some researchers use carbon material as a place to deposit cobalt, besides being cheap, carbon is also easy to obtain [7, 8]. A comprehensive review of the use of cobalt as a phosphate potentiometric sensor has now been reported [9].

## 2   Materials and Method

### 2.1   Cobalt-Carbon Electrode Development

$Co^{2+}$ source electrolyte solution was prepared from 50 mL of 0.01 M $CoSO_4 \cdot 7H_2O$ solution and 10 mL of 1 M $(NH_4)_2SO_4$ solution, the pH of the solution was adjusted to 6 by adding 0.02 M $NH_4OH$ dropwise. Electrodeposition by voltammetry was carried out on carbon working electrodes, Ag/AgCl as reference electrodes, and stainless steel as auxiliary electrodes. The voltammetry process was carried out in the potential area of 0 to $-1000$ mV with a scan rate of 1 mV/s, using a potentiostat (AMEL 433A). Polarization of the working electrode is carried out with two models, namely Cyclic Voltammetry and Linear Sweep Voltammetry. The surface of the cobalt deposit on the carbon was then characterized by morphology using SEM, besides that, potentiometric characterization was also carried out.

### 2.2   Measurement of Cobalt Levels in Solution by Spectrophotometry

To confirm the occurrence of cobalt reduction in the deposition source solution, a quantitative test of the cobalt content was carried out spectrometrically [10]. The solution before the deposition was taken 2 mL then put into a 10 mL volumetric flask and added 0.8 mL of 6 M HCL, 2 mL of 50% KSCN, and 4.8 mL of acetone. The mixture is added with distilled water up to the limit mark. The solution mixture was homogenized, then allowed to stand for 30 min. The absorbance measurement was carried out by inserting the solution into a cuvette along with a blank in the form of distilled water, then measured with a UV-Vis spectrometer at a wavelength of 620 nm. Measurements were carried out 3 times. Measurement of the solution after deposition was also carried out with the same procedure.

### 2.3   Potentiometric Characterization of Cobalt-Carbon Electrode Performance

Performance assessment of cobalt-carbon electrode in potentiometric phosphate measurement was carried out by taking 10 mL of 0.01 concentration of phosphate standard

solution; 0.1; 1; 10; 100 ppm. The solution was put into a beaker and added ISA KHP 0.2 mL pH 4 solution at each concentration [11]. The cobalt-carbon electrode and the Ag/AgCl electrode were then immersed in a solution previously homogenized with a magnetic stirrer and the potential difference was read using a pH/mVmeter (Jenway). The potential measurement at each concentration of the standard solution was repeated three times. Data processing to obtain a calibration curve is done by plotting the x-axis as the concentration log and the y-axis as the potential difference. The evaluated cobalt-carbon electrode performance parameters were working area, detection limit, sensitivity, and reproducibility.

## 3    Result and Discussion

### 3.1   Electrodeposition Process

Figure 1 is a voltammogram of cobalt electrodeposition on the surface of a carbon rod by cyclic voltammetry. The results obtained indicate that there has been an oxidation and reduction reaction of the cobalt in the solution. The voltammogram shows the reduction of $Co^{2+}$ to Co at a potential of $-770$ to $-805$ mV and oxidation occurs in the potential area of around $-385$ to $-410$ mV for the 1st cycle electrodeposition. Voltammogram Fig. 1 also shows the formation of oxidation peaks in the potential region around $-445$ to $-465$ mV for the 2nd cycle electrodeposition and $-335$ to $-355$ mV for the 3rd cycle electrodeposition. The formation of a reduction peak occurs in the potential area around $-885$ to $-905$ mV with a peak current of $-5,845$ µA for the 2nd cycle of electrodeposition and $-875$ to $-895$ mV with a peak current of $-5,125$ µA for the 3rd cycle of electrodeposition. This result was in-line with Kiruba & Jeyabharathi (2020) which the reduction of cobalt was electrodeposited by diffusion-controlled reduction reaction $-870$ mV [12]. Meanwhile, other researchers also showed a potential in the $-800$ mV region on the voltammogram for electrodeposition of cobalt with cobalt chloride material and ammonium chloride electrolyte solution which was carried out with a carbon ultramicroelectrode and a scan rate of 30 mV/s [13].

Figure 2 is a voltammogram of cobalt electrodeposition on the surface of a carbon rod by linear sweep voltammetry. The results obtained indicate that there has been a reduction reaction of the cobalt. The voltammogram shows the formation of a reduction peak in the potential region around $-735$ to $-745$ mV with a peak current of $-8585$ µA for the 1st cycle electrodeposition. In the potential area around $-735$ to $-745$ mV, the reaction that occurs is the reduction of cobalt ions. Electrodeposition by linear sweep voltammetry method also showed the formation of reduction peaks in the potential area around $-730$ to $-750$ mV with a peak current of $-9105$ µA for the 2nd cycle of electrodeposition and $-745$ to $-785$ mV with a peak current of $-18770$ µA for the 3rd cycle.

### 3.2   Electrodes Surface Morphological Analysis

Morphological examination with SEM of the electrodeposition results showed clearly different results when compared to the carbon surface before electrodeposition. Prior to
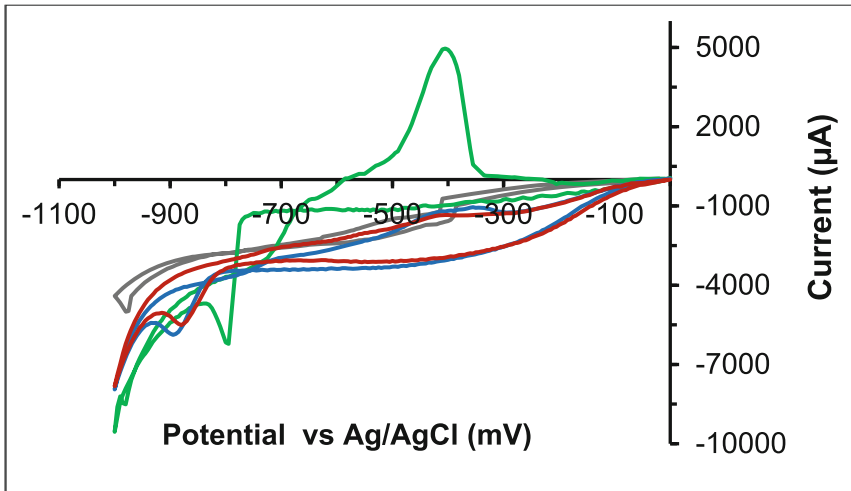
**Fig. 1.** Voltammogram of electrodeposition process in cyclic voltammetry (CV) mode
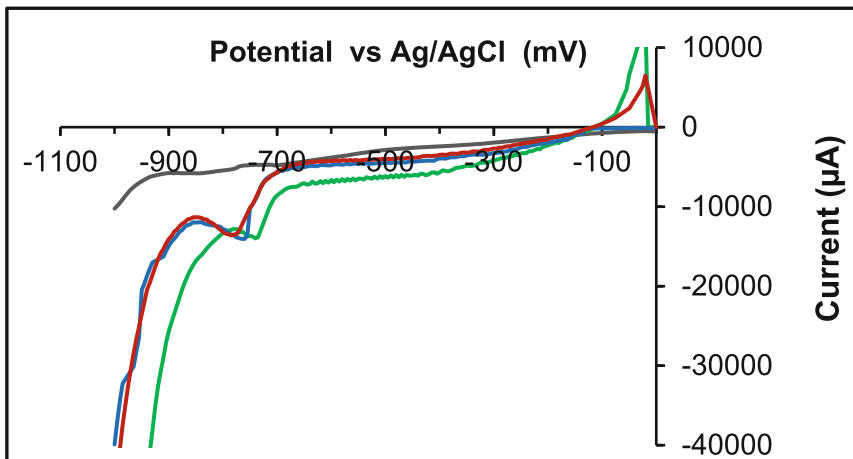


**Fig. 2.** Voltammogram of electrodeposition process using linear sweep voltammetry (LSV) technique

electrodeposition, the cavities shown in Fig. 3(a) were large and smooth. The morphological structure formed in the image shows cavities that are not too tight, so it looks like there is a gap (black hole). Figure 3(b) shows the surface morphology of the carbon electrode after being electrodeposited using the cyclic voltammetry method which shows a smaller and denser cavity size than the carbon electrode (Fig. 3(a)), an uneven surface, and a rougher physical appearance than the carbon electrode. The surface morphology of the electrode in Fig. 3(c), which uses a linear sweep voltammetry method, shows a smaller and more uniform cavity size than the carbon electrode, a denser surface, and a rougher physical appearance.
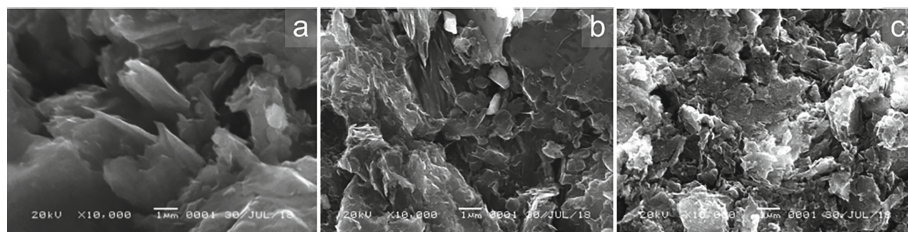
**Fig. 3.** Surface morphology structure of electrodes (a) control electrode, (b) CV-based electrode, and (c) LSV-based electrode

**Table 1.** Measurement results of cobalt in solutions undergoing CV polarization

| Electrodeposition | [Co] deposited (mol/L) | m Co deposited (gram) |
|---|---|---|
| 1 | $4.2 \times 10^{-4}$ | $5.90 \times 10^{-3}$ |
| 2 | $3.9 \times 10^{-4}$ | $5.47 \times 10^{-3}$ |
| 3 | $3.4 \times 10^{-4}$ | $4.77 \times 10^{-3}$ |

**Table 2.** Measurement results of cobalt in solutions undergoing LSV polarization

| Electrodeposition | [Co] deposited (mol/L) | m Co deposited (gram) |
|---|---|---|
| 1 | $6.0 \times 10^{-4}$ | $8.43 \times 10^{-3}$ |
| 2 | $5.9 \times 10^{-4}$ | $8.28 \times 10^{-3}$ |
| 3 | $5.1 \times 10^{-4}$ | $7.16 \times 10^{-3}$ |

## 3.3   Measurement of Residual Cobalt in Solution

Based on the analysis of cobalt content in the solution (Tables 1 and 2), the mass of cobalt deposited on the surface of the carbon rods using the LSV method was higher than the CV method. This can be caused by differences in the electrodeposition process in the two voltammetry methods, namely the electrode polarization process which only accommodates the reduction reaction in the LSV method so that the deposited Co sticks more firmly without the possibility of turning into $Co^{2+}$ again. This is also confirmed by the characterization data using the SEM method which shows that the cobalt deposited on the surface of the carbon rods by the LSV method seems more abundant and has better morphology than the electrodes from the CV method.

## 3.4   Potentiometric Performance of the Electrodes

The potentiometric performance of the cobalt-carbon electrode was measured from the linearity of the plot between log [phosphate concentration] and the potential response of the electrode. The linear region of the cobalt-carbon electrode prepared by the electrodeposition process using the cyclic voltammetry method for detecting phosphate is shown

in Fig. 4(a), which shows that the cobalt-carbon electrode for detecting phosphate with a concentration of 0.01; 0.1; 1; 10; and 100 ppm are in the linear region with a correlation of 0.995. Meanwhile, the cobalt-carbon electrodes made through the electrodeposition process using the linear sweep voltammetry method (Fig. 4b) showed that in the same range of phosphate concentrations, a correlation coefficient of 0.998 was obtained. The results obtained using the linear sweep voltammetry method were slightly better than the cyclic voltammetry method. The performance of the electrode that is very clearly different is the sensitivity, namely the electrode produced by LSV gives a sensitivity value of 31.70 mV/decade while that which is produced by CV is only 26.78 mV/decade. It is strongly assumed that the number of deposited cobalt layers is directly correlated to the sensitivity.

On consecutive observations for 7 days, it was found that there was a decrease in the sensitivity value (Fig. 5) for both electrodes. It is assumed that the cobalt layer on the carbon underwent changes during this period. The response of the cobalt-carbon electrode was the best overall on the first day of use.

Based on the measurement results, as shown in Fig. 6, the lowest coefficient of variance for the 1st deposition is 0.07% at a concentration of 10 ppm, while the highest coefficient of variance is 0.68% at a concentration of 0.01 ppm. These data indicate that the repeatability of the cobalt-carbon electrode deposited by the cyclic voltammetry method for phosphate analysis is good because the CoV value is less than 5%. On the other hand, observations of LSV-based electrodes resulted in the lowest coefficient of variation of 0.29% at a concentration of 0.01 ppm, while the highest coefficient of variation was 0.65% at a concentration of 0.1 ppm. These data indicate that the repeatability of the cobalt-carbon electrode deposited by the linear sweep voltammetry method for phosphate analysis is good because the CoV value is less than 5%.
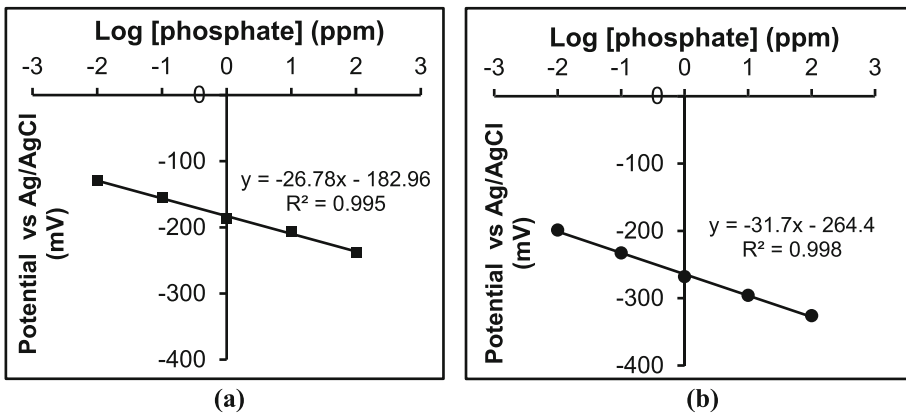


**Fig. 4.** Potential response of cobalt-carbon electrodes in measuring variations in phosphate concentration: (a) deposited Cyclic Voltammetry, (b) deposited Linear Sweep Voltammetry
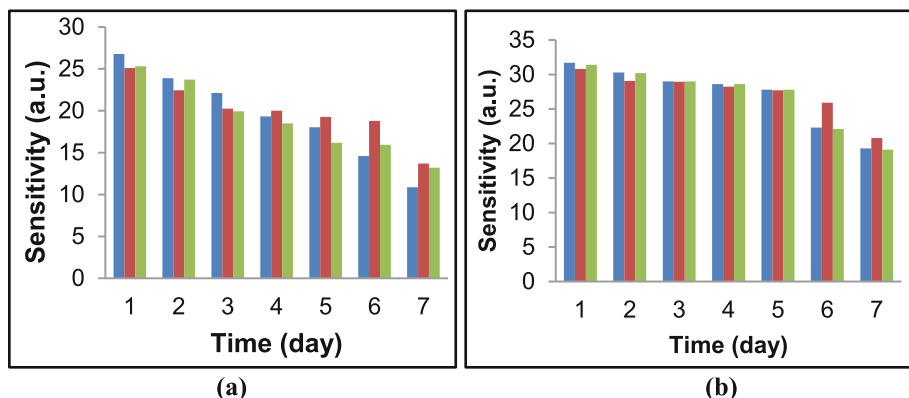
**Fig. 5.** Sensitivity degradation of CV-based (a) and LSV-based electrodes (b) for 7 days of observation in (■ 1st electrode; ■ 2nd electrode; ■ 3rd electrode)
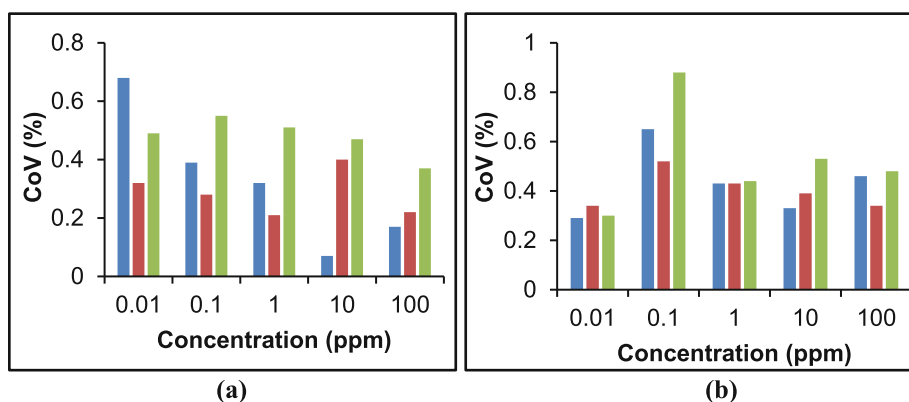


**Fig. 6.** Coefficient of variance of CV-based electrode (a) and LSV-based electrode (b) at various phosphate concentrations in (■ 1st electrode; ■ 2nd electrode; ■ 3rd electrode)

## 4   Conclusion

Cobalt electrodeposition from cobalt sulfate solution on carbon electrodes by Linear Sweep Voltammetry method showed better results than electrodeposition by Cyclic Voltammetry method. These results are supported by data from SEM analysis and analysis of the amount of phosphate deposited. The performance of the cobalt-carbon electrode in measuring phosphate potentiometrically showed the following results: linear region at a concentration of 0.01 ppm to 100 ppm, the detection limit of 1.43 ppm, sensitivity value of 31.7 mV/decade, and reproducibility seen of the coefficient of variation values ranged between 0.07% and 0.68%.

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