Electrochemical Study of Modified Iron Electrode for Anion Determination

Mulyawati1, Kartika A. Madurani1, E. Fitriany1, I. Ulfin1, A. Tanjung2, L. Devy2, D. Maretta2, F.Kurniawan 1\*

1Department of Chemistry, Faculty of Science and Data Analytics, Institut Teknologi Sepuluh Nopember Surabaya (ITS), Surabaya, Indonesia, 60111.

2Research Center for Horticulture, National Research and Innovation Agency, Cibinong Science Center, Bogor, Indonesia, 16915

\* fredy@chem.its.ac.id

**Abstract.** An oxalate ion has been successfully determined using a modified iron electrode. The electrode was made by depositing a more corrosion-resistant metal on the iron surface. Comparison results of the electrode with and without modification were studied. The performance of the electrode was investigated by measuring oxalate acid 0.04 M in 0.05 M H2SO4 using the cyclic voltammetry (CV) method. The measurement was conducted in the potential range of -0.4 to 0.4 V, with various scan rates also studied. The modified Fe electrode demonstrated an excellent selectivity for oxalate acid detection. Cyclic voltammetry measurements of various interfering components did not show oxidation-reduction activity. These findings confirm that the modified iron electrode is effective for a selective electrochemical sensor in oxalic acid determination.   
  
**Keywords:** *Electrochemical, Iron, Oxalate acid, Selective sensor.*

# INTRODUCTION

Oxalate is a divalent organic anion that plays a significant role in many biological and commercial processes. This anion is derived from plants such as spinach, tea, cocoa, and legumes. Hence, it is frequently found in both raw and processed food products [1]. Although oxalate has certain physiological benefits, excessive consumption can have detrimental effects on health. Elevated oxalate levels can induce oxidative stress, kidney epithelial cell damage, and inflammation due to an increase in reactive oxygen species and a reduction in glutathione levels. This not only promotes the formation of calcium oxalate stones in the kidneys but also disrupts the body’s natural mechanisms for clearing oxalate crystals. Specifically, it impairs the differentiation of monocytes into macrophages, which are essential for the clearance of oxalate crystals and the maintenance of kidney health [2], [3]. In addition, high oxalate levels can lower blood calcium levels, potentially disrupting heart and nervous system function [4]. The body's immune response can also be impaired due to excessive oxalate exposure, even in healthy individuals. Calcium oxalate crystals are found at various taxonomic levels in photosynthetic organisms. However, challenges arise in reporting oxalate content in food due to inaccuracies in the analytical methods employed. Therefore, accurate measurement of oxalic acid becomes crucial, not only to support a balanced dietary regimen by limiting oxalate intake to around 50–100 mg per day but also to ensure food product quality. Additionally, monitoring oxalate content is an important step in the diagnosis and prevention of kidney stone formation, making it a significant parameter in maintaining health and managing medical risks [5].

Research on oxalate concentration in biological fluids such as urine and blood can aid in the investigation, diagnosis, and medical management of various clinical disorders/diseases, including chronic kidney disease, primary hyperoxaluria, intestinal malabsorption, nephrolithiasis, steatorrhea, and ileal disease [6]. In addition, the analysis of oxalate content in food samples is also crucial for monitoring oxalate intake, which can impact health. Several methods have been employed for this purpose, including enzymatic assays [7], [8], spectrofluorimetry [9], capillary electrophoresis [10], [11], gas chromatography (GC) [12], and high-performance liquid chromatography (HPLC) [13]. Although these methods provide accurate and reliable results, they are reported to require pretreatment, are costly, and may introduce significant inaccuracies if sample handling and measurement are not carefully executed [14]. In comparison to other techniques, electrochemical sensor methods stand out due to their affordability, ease of operation, environmental friendliness, high sensitivity, and suitability for field testing [15]. The fundamental principle of electrochemical detection relies on oxidation-reduction processes. Noble metal electrodes, such as Pt [16] and Au [17], are commonly used as the core of these systems. Noble metal-based materials are widely recognized as the most efficient in various electrochemical applications due to their high electrical conductivity, excellent stability, and outstanding electrocatalytic activity. However, the scarcity and high cost of noble metals remain significant challenges, limiting their utilization and driving the development of alternative materials that are more abundant, cost-effective, easily accessible, and exhibit high activity and stability [18], [19]. In contrast, iron and copper are more affordable and show substantial potential as sensor materials. Sensors based on a combination of iron and copper offer several advantages, including low production costs and simple fabrication processes. The high electrical conductivity and catalytic properties of copper are expected to enhance the sensitivity and stability of the electrode, while iron, as the core material, provides mechanical strength and structural stability. This combination is anticipated to produce electrodes with optimal performance in terms of detection limit, sensitivity, reproducibility, and repeatability for oxalate ion detection, making them suitable for applications in chemical analysis and biomedical fields.

# matERIALs AND METHODS

## Materials

Iron (Fe) metal was sourced from the local market, while copper(II) sulfate pentahydrate (CuSO₄·5H₂O), sulfuric acid (H₂SO₄), and oxalic acid dihydrate (C₂H₂O₄·2H₂O) were purchased from Sigma-Aldrich, USA. D-(+)-Glucose anhydrous (C₆H₁₂O₆), ascorbic acid, and uric acid were also purchased from PT. Smart Lab Indonesia. Deionized water (Aqua DM) was supplied by PT. Brataco Indonesia.

## Preparation of Modified Electrode

The iron modified electrode was prepared using a chemical deposition method. Initially, a clean iron (Fe) substrate was meticulously prepared by removing any rust and ensuring its pristine condition. Copper (Cu) was deposited onto the iron surface. The deposition process was carefully controlled to achieve a uniform copper coating. After deposition, the electrode was rinsed thoroughly with deionized water to remove any residual chemicals and air-dried under ambient conditions. The electrochemical properties of the bimetallic electrode were evaluated using cyclic voltammetry (CV).

## Electrochemical Sensing

The electrochemical performance of the modified electrode was evaluated using cyclic voltammetry (CV) with an Autolab PGSTAT128N potentiostat, equipped with Nova software version 2.1.6. A three-electrode system was employed, where the copper-modified iron electrode served as the working electrode, an Ag/AgCl electrode was used as the reference electrode, and a platinum wire acted as the counter electrode. The electrolyte solution consisted of 0.05 M sulfuric acid (H₂SO₄). Cyclic voltammetry measurements were conducted over a potential range of -0.4 to 0.4 V (vs. Ag/AgCl) at a scan rate of 100 mV/s, ensuring precise characterization of the electrode's electrochemical properties.

# RESULTS AND DISCUSSIONS

## Electrocatalytic Oxidation of Oxalate Ion at Different Electrode

The electrochemical response of the modified electrode towards oxalate was investigated using cyclic voltammetry (CV) to explore the electrocatalytic effect of modified and unmodified electrodes on oxalate oxidation. Figure 1 illustrates the CV curves of the bare Fe and copper modified iron electrodes at a scan rate of 100 mV/s in a solution of 0.04 M H2C2O4 in 0.05 M H2SO4. The current response of the bare Fe electrode shows no significant anodic peak, whereas the copper modified iron electrode exhibits a distinct current response with an anodic peak at around +0.196 V potential. This observation suggests that the Cu modification likely provides a synergistic effect in enhancing the sensitive detection of oxalate.

Oxalate, in the form of oxalic acid (OA), has limited absorptive ability with the bare Fe electrode, thus retarding the oxidation process at the surface. However, metals catalyze the oxidation process. Therefore, oxalate can undergo electrochemical oxidation on the bimetallic copper modified iron electrode surface. With the metal, the reaction mechanism involves electro-oxidation of oxalate, which produces carbon dioxide and hydrogen ions. It has been reported that the oxidation of oxalate is based on a two-electron, two-proton mechanism to form carbon dioxide [20]. The proposed reaction is given below (1):

H2C2O4 → 2CO2+ 2H+ + 2e− (1)

This reaction occurs at the electrode, where electrons released from the oxidation of oxalate are captured by copper modified iron electrode. Cu processes good conductivity and catalytic activity for oxalate detection, thereby accelerating the oxidation process of oxalate at the electrode.



**Figure 1.** Cyclic voltammogram of the Fe electrode (black) and copper modified iron electrode (red) in 0.05 M H2SO4, scan rate 100 mV/s and potential range of -0.4 V to 0.4 V

## The Effect of Scan Rate

The effect of scan rate was investigated to determine whether the process occurring is governed by diffusion or adsorption [21]. The effect of scan rate on the oxidation and reduction of oxalate on the copper modified iron electrode was examined using CV. The measurements were conducted on 0.04 M H2C2O4 in 0.05 M H2SO4 at various scan rates (30-200 mV/s) (Figure 2A). As illustrated in Figure 2A, the peak current gradually increases with the increment of the scan rate. The comparison of the anodic and cathodic current values (ipa/ipc) is less than 1, indicating that the electrochemical process is quasi-reversible. Therefore, there is a proportional relationship between ∆Ep [∆Ep – Epc] and the scan rate, where the oxidation process shifts towards more positive potentials, while the reduction current shifts towards more negative potentials with increasing scan rate [22]. The increase in ∆Ep with the rising scan rate indicates the presence of kinetic limitations in charge transfer during the electrochemical process [23].

The diffusion controlled mass transfer process of copper modified iron electrodes was investigated. As shown in Figure 2B, both cathodic and anodic peak current responses are directly proportional to the square root of scan rate (v1/2), and the linearization equation (2) is as follows:

Ipa = 0.716 (v1/2) – 1.929 (R2 = 0.99056) (2)

The Randles-Servick equation (3) indicated that a diffusion controlled mass transfer process occurs on copper modified iron electrodes.

Ip = (2.69 x 105) n3/2 AD1/2 v1/2 C (3)

Where n is the electron exchange number of the redox reaction, and A is the active area of the working electrode (cm2). The diffusion coefficient (D (cm2 s-1)) and the bulk concentration of the electroactive species is C (mol cm-3). The voltage scan rate (V s-1) is v



**Figure 2.** Cyclic voltammogram 0.04 M oxalate ion obtained by copper modified iron electrode in 0.05 M H2SO4,at different scan rates (30, 50, 75, 100, 150, and 200 mV/s) (A) and plot of anodic current at vs square root of the scan rate (B).

## Electrochemical detection of oxalate

Cyclic voltammetry (CV) was used to study the analytical performance at a scan rate of 100 mV/s in 0.05 M H2SO4 with various oxalate concentrations (Figure 3A). In the studied potential scanning range, no redox peaks were observed on the surface of copper modified iron electrode, indicating the stability of the electrode. However, after the addition of oxalate, a significant anodic peak appeared at a potential of +0.189 V, indicating the presence of a typical electrocatalytic oxidation process of oxalate. The anodic current was linear along with the oxalate concentration in the range of 10 – 80 mM and the coefficient of linearity (R2) was found to be 0.99343. As depicted in Figure 3B, along with the increase oxalate concentration, the maximum oxidation current (ipa) on the copper modified iron electrode increased proportionally, and its linear regression equation is (4):

Ipa = 0.02169[H2C2O4] + 2.55284 (R2 = 0.99343) (4)



**Figure 3.** Cyclic voltammogram at various concentrations of oxalate ion in 0.05 M H2SO4 by copper modified iron electrode (A) and plot of anodic current vs concentrations (B).

## Interference Study

We conducted interference measurements to evaluate the selectivity of the proposed sensor. Common biological species, including 0.04 M uric acid, 0.04 M glucose, and 0.04 M ascorbic acid, were studied on the copper modified iron electrode within the potential range for oxalate detection. Figure 4 depicts the CV current response to these compounds using the developed electrode. The sensor only exhibited a significant response to oxalate and did not show redox peaks for other ions. Therefore, it can be concluded that the copper modified iron electrode demonstrates good selectivity.



**Figure 4.** Interference study of the modified electrode

# CONCLUSION

A simple chemical deposition method was used to prepare an electrochemical sensor based on iron and copper metals, which was then applied for oxalate detection. The prepared copper modified iron electrode demonstrated excellent electrocatalytic ability for oxalate detection with a LOD of 0.56 mM. the reaction on the electrode surface is diffusion-controlled. The performance of the copper-modified iron electrode for oxalate detection remains unaffected by the presence of glucose, uric acid, and ascorbic acid, indicating its high selectivity for oxalate determination. Moreover, the proposed method offers advantages such as simple pretreatment, no requirement for complex reagents, and low cost.

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