Preliminary Study of Oxidation and Reduction for Oxalate Ion Detection

E Fitriany1,a), Mulyawati1,b), F Kurniawan1\*,c)

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

a)[7004232005@student.its.ac.id](mailto:7004232005@student.its.ac.id)

b)[mulyawati0102@gmail.com](mailto:mulyawati0102@gmail.com)

\*c) [fredy@chem.its.ac.id](mailto:fredy@chem.its.ac.id)

**Abstract.** The modified iron electrode for detecting oxalate ions was successfully developed. The iron electrode was made by immersing it in a 0.5 M CuSO4 solution. The immersion is carried out using a specific time variation. The iron electrode has been coated and then placed in 50% H2O2 solution to accelerate the oxidation reaction on the electrode surface. The performance of the modified electrode was carried out using the cyclic voltammetry method at a potential range of -0.4 to +0.5 V. Iron electrode without modification was used for comparison study. The result shows no oxidation and reduction peak using an iron electrode without modification, while oxidation and reduction peak appeared at +0.08 V and +0.07 V, respectively, using the modified iron electrode. This data means that the modified iron electrode is sensitive to oxalate ions. The scan rate was varied at 25: 50; 75; 100; and 150 mVs-1. The result showed that the optimum scan rate is 100 mVs-1. The measurement of 0; 1; 2; 3; 4; 5 mM oxalic ion have also been conducted, showing a linear increase in current (A). The equation is y= 0.0023x +0.0004, R2= 0.9918. The LOD is 6.2 x 10-1 mM. This modified electrode is selective toward ascorbic acid, uric acid, and glucose interference. These findings indicate that modified iron electrodes can detect oxalate ions.

**Keywords**: *Electrochemical sensors, Iron electrode, Metal oxide, Oxalate.*

# INTRODUCTION

Oxalate is an anion with the chemical formula C2O4-2, a product of protein metabolism apart from food consumption, which is then excreted by the kidneys through urine [1]. Oxalate can react with cations such as sodium and calcium, often as insoluble sodium or calcium oxalate in the blood [2][3]. The presence of oxalate in human urine can be used as an indication of hyperoxaluria and increases the risk of various health problems such as kidney stones, kidney failure, inhibition of nutrient absorption, and inhibition of treatment effectiveness. The maximum oxalate content consumed in food is 50 mg/day [4][5]. Therefore, measuring oxalate in food is very important. Excess oxalate ions in humans are usually detected through blood and urine, where the average oxalate concentrations are 1-5 mM and <460 mM, respectively [1]. Oxalic acid analysis can be carried out using various methods, such as High-Performance Liquid Chromatography (HPLC), ion exclusion chromatography, Gas Chromatography (GC), Atomic Absorption Spectroscopy (AAS), permanganometry titration, and UV-Vis spectrophotometry [6]. These methods have several areas for improvement, including long analysis times, long and complex sample preparation, not being economical, and low accuracy and sensitivity. This research will develop an electrochemical method that considers the potential for fast, economical, accurate, selective, and sensitive sample analysis. The field of electrochemistry is one solution for developing electrochemical sensors. Various electrochemical sensors for analysing oxalate ions in food samples have been developed, including the development of PdNPs, AuNPs, and PtNPs electrodes, which have low detection limits [1]. However, some of the electrodes that have been developed need to improve in terms of their economic value. The electrochemical sensor developed in this research is made from iron modified using pure copper metal; iron and copper will stabilize each other. Iron and copper have good electrical conductivity properties, so researchers will utilize this potential to develop working electrodes. Apart from that, the basic materials used have economic value and are easy to obtain domestically. Electrode performance will be tested using a potentiostat/galvanostat to determine sensitivity, measurement area, detection limit, precision and accuracy. Research related to the development of working electrodes will continue to be carried out due to the overlapping peaks of oxidation potential between uric acid, ascorbic acid, and oxalic acid when carbon paste electrodes are used without modification in future research. This research's problem is finding alternative electrodes that are more economical and have higher performance than the existing ones. The proposed electrode is copper-modified iron.

**MATERIAL AND METHODS**

## Chemicals

Bare Fe, Hydrogen Peroxide (H2O2) was obtained from Sigma Aldrich, Deionized water from Bioanalitika, CuSO4. 5H2O from Sigma Aldrich, Oxalic Acid (H2C2O4) from Merck, Sulfuric Acid (H2SO4) from Sigma Aldrich, and other chemicals from Sigma Aldrich. All reagents were of analytical quality.

**Preparation of Iron Modified Electrode**

Modified iron electrodes are made by preparing rust-free 5 cm iron rods. The iron rod coated with metal oxide is then placed in a short time in a 50% H2O2 solution. The metal oxide-modified iron electrode is then analyzed for its performance using cyclic voltammetry.

**Electrochemical Measurements**

Electrochemical measurements were performed by AUTOLAB PGSTAT-13 electrochemical workstation (Eco-Chemie, The Netherlands). A standard three-electrode electrochemical cell was used. The working electrode is a modified electrode, with Ag/AgCl (sat) as the reference electrode, and a Pt wire as a counter electrode. The potential in all figures is indicated relative to this reference electrode. The measurements were performed at various concentrations of H2C2O4 in 0.05 M H2SO4.  Scan rate optimization in this study was carried out by varying the scan rate starting from 25 mV/s; 50 mV/s; 75 mV/s; 100 mV/s; and 100 mV/s. This stage determines the best scan rate which will then be used in subsequent measurements. Determination of detection limits and sensitivity, as well as electrochemical reactions on the electrode surface, was carried out by varying the concentration of H2C2O4 : 1 mM; 2 mM; 3 mM; 4 mM; and 5 mM in 0.05 M H2SO4.

**RESULT**

**Modified iron electrode coated with metal oxide**

****This research uses a combination of Fe and metal oxides as electrochemical oxalate sensors. Bare Fe has a dark grey colour. The bare Fe electrode used to measure H2C2O4 did not produce oxidation or reduction peaks. An unmodified iron electrode dipped in an H2C2O4 solution for 5 minutes will experience oxidation on its surface, which is indicated by the blackening of the electrode surface. The electrode developed in this research is a combination of Bare Fe and metal oxide of Cu. Bare Fe, coated with metal oxide, has a dark red colour and better stability in H2C2O4 measurements (Figure 1).

**FIGURE 1.** Cyclic voltammogram of the Fe electrode and Fe with modification electrode in 0.05 M H2SO4, scan rate 0.1V and potential range of -0.4 V to +0.5V.

**Effect of Scan Rate**

The scan rate effect in this study was carried out by measuring H2C2O4 in 0.05 M H2SO4 at various concentrations. Based on the voltammogram data (Fig. 2), it can be seen that the higher the scan rate used in the measurement, the higher the current obtained. Scan rate optimization was done by calculating the Ipa/Ipc value closest to 1. Based on the calculation results, it was found that the Ipa/Ipc value that was closest to 1 was at a scan rate of 100 mV/s. Measurements in the next stage used a scan rate of 100 mV/s.

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**FIGURE 2.** Cyclic voltammogram scan rate optimisation of oxalate ions

**Electrochemical properties of oxalate**

The analysis of the electrochemical response of oxalate oxidation and reduction at two different electrodes (unmodified and modified Fe electrodes). All measurements are performed in the H2SO4 solution as a supporting electrolyte. The cyclic voltammogram of oxalate ion over a concentration range of 1 mM to 5 mM in H2SO4 solution can be seen in Fig 3. The peak of oxidation and reduction increases as the oxalate ion concentration rises from 1 mM to 5 mM.

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**FIGURE 3**. Cyclic voltammogram at various concentrations of oxalate ion in 0.05 M H2SO4 at scan rate 100 mV/s by Fe-modified electrode

**DISCUSSION**

**Modified iron electrode coated with metal oxide**

Iron electrodes that are modified using metal oxide will have a higher stability and performance when compared to iron electrodes without modification. Metal oxide coated on the surface of iron electrodes has several advantages, including being non-toxic, a suitable semiconductor, cheap, and relatively stable from a chemical and physical perspective. It has wide applications in electrochemistry [7]. The size of the metal oxide particles is relatively smaller than that of the original metal, so the surface area used to sensor the analyte will be more significant and influential [8][9]. Metal oxides have low electrical conductivity, so in this research, a combination of metal oxide-coated iron electrodes was used to improve the electrical quality and increase the corrosion resistance of the iron surface. The fabrication process of the modified electrode was ion-exchange, and in-situ growth occurred with Fe as a precursor, then the metal oxide ions migrated to the surface of Fe. The oxidation process continued when the electrode was dipped into the H2O2 solution with a certain concentration. After this process, the metal oxide will be coated on the outer layer of Fe. Cu is an excellent material for oxalate and acidic solutions' cathodic and anodic reduction. Besides that, Cu-Oxide (metal oxide) has the advantages of nontoxicity, excellent conductivity, and low-cost material. Increasing studies have proven that metals with Cu alloys, e.g., Cu-Pd [10], Cu-Ni [11], Cu-Ag [12], and Cu-Rh [13] can be efficient for various applications. Regarding its performance on oxalate ions, Fe- metal oxide-based electrodes exhibit an expeditious current decay and inherently large pores that can withstand high stable current values. This modified iron electrode shows oxidation and reduction peaks when used to measure H2C2O4 in a 0.05 M H2SO4 solution. This indicates that the Fe electrode modified with metal oxide performs better than the unmodified Fe electrode. Based on this data, we can suggest that the modified electrode is better to transfer the electron than the unmodified electrode. On the other hand, the modified electrode developed has better oxidation and reduction peaks than the electrode without modification. This reaction can be used for quantitative analysis, such as the study of interference and the mechanism reaction.

H2C2O4 + 2e- 🡪 2Co2  (1)

The proposed mechanisms are proposed below:

C2O42--e 🡪C2O42. (2)

C2O42. 🡪 CO2 + CO-.2 (3)

1[CO-.↑2 + CO-. ½ ] 🡪 C2O42- (4)

3[CO-.↑2 + CO-.↑2 ] ≠ C2O42- (5)

CO-.2-e 🡪 CO2 (6)

The reduction reaction of oxygen is as follows:

O2 + 2H+ + 2e- 🡺 H2O2 , Eo = +0,695 V

**Electrochemical properties of oxalate on modified iron electrodes**

The electrochemical properties of oxalate ions were studied using cyclic voltammetry techniques. The electrodes used in this research were unmodified Fe electrodes and metal oxide-modified Fe electrodes. Electrode variations are intended to determine the speed of electron transfer by the analyte on the electrode surface. Oxalate ion measurements were carried out at an oxalate concentration of 1 mM; 2 mM; 3 mM; 4 mM; and 5 mM in 0.05 M H2SO4. Cyclic voltammetry measurements were carried out in the potential range of -0.4 V to +0.5 V with a scan rate of 0.1 V. Fig.1 Shows differences between unmodified Fe electrodes and modified Fe electrodes. The unmodified Fe electrode does not show oxidation and reduction peaks when used to sensor oxalate. However, the modified Fe electrode showed apparent oxidation and reduction peaks of oxalate ions. This proves the developed electrode has more sensitive properties than the unmodified Fe electrode. The appearance of oxidation and reduction peaks of oxalate ions on the modified Fe electrode indicates the synergy between Fe and metal oxides, thereby increasing the catalytic effect of the electrode surface. Metal oxides have good electrocatalytic properties, so modified Fe electrodes can be used to sensor oxalate ions [11].

**Effect of scan rate**

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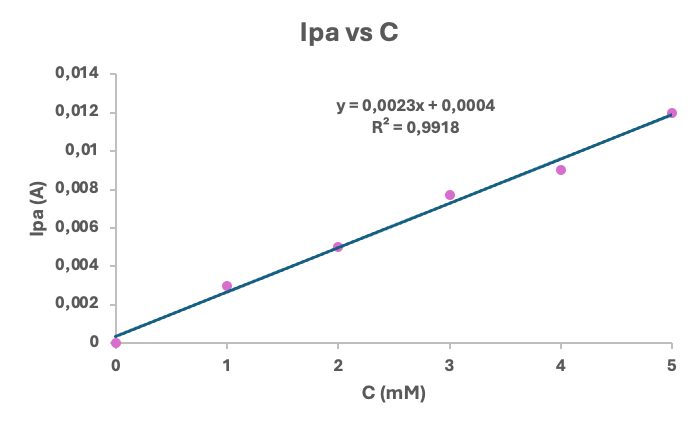
Description automatically generated with medium confidenceMeasurements were carried out using a solution of 0.2 mM oxalate in 0.05 M H2SO4. The oxalate ion scan rate was varied by 25, 50, 75, 100, and 150 mVs-1. The potential range used in this research is -0.4 V to +0.5 V. Measurements were carried out three times for each scan rate. The increase in oxalate ions' anodic and cathodic peak currents is linear with the increase in scan rate. The resulting diffusion layer will be thinner and the transfer of electrons on the surface of the modified Fe electrode will be faster. On the other hand, at a small scan rate, the thickness of the diffusion layer is produced, which inhibits the electron transfer process on the surface of the electrode, and the resulting peak current is small [14][15]. The effect of scan rate in this research was studied to determine the reaction mechanism on the surface of the modified Fe electrode, whether controlled by adsorption or diffusion processes.

**FIGURE 4.** Plots between the anodic peak current (Ipa) and V1/2.

The Ipa is plotted against v1/2, which has a linear correlation. Based on this data, we can correlate it with Randles Sevcik’s equation; the reaction is diffusion-controlled. The linear equation is Ipa = 3.6798 (v1/2) + 0.2547 with R2= 0.9904. Based on this equation, the diffusion coefficient is 2.54 x 10-6 cm2 s-1, where Ipa is the anodic peak current of oxalate ions (A). N is the accumulated electron involved in the reaction, A is the area of the modified electrode, C is the oxalate ions concentration mol/ cm3, and v is the scan rate (V/s). The optimum scan rate is determined based on the Ipa/Ipc value close to 1. In this study, the optimum scan rate was 100 mVs-1.

**Sensitivity of the modified electrode**

Linearity is the ability of a method to provide proportional results over analyte concentrations within a certain range. The correlation coefficient (R2) value on the standard curve is tested with t, which shows the linearity parameter produced by a method. Based on the curve of the relationship between concentration and peak anodic current in oxalate ion analysis, it was found that the linear equation is Y= 0.0023x + 0.0004, with the correlation of R2 being 0.9918, which is close to 1. This shows that the linearity value produced by this method is relatively good. measurements were carried out at a concentration of 1mM; 2 mM; 3 mM; 4 mM; and 5 mM.



**FIGURE 5.** Plots between the anodic peak current (Ipa) and various concentrations (C).

The slope resulting from the standard curve shows the sensitivity of the analytical method developed. The slope value obtained is 0.0023. The limit of detection is 6.2 x 10-1 mM.

**Selectivity of the modified electrode**

The effects of several interferents were explored in this study: ascorbic acid, uric acid, and glucose were observed. Based on Figure 6, we can see no peaks were detected for the analysis of ascorbic acid, uric acid and glucose using the modified electrode that has been developed. The measurement potential is -0,4 V to +0,5 V. Additions for oxalate ions are 1 mM and 5 mM for ascorbic acid, uric acid, and glucose. There is an increasing current for oxalate ion addition but no response for other compounds, although the concentration is 5 times higher. The modified electrode can only sensor oxalic acid. This modified electrode was selective.

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**FIGURE 6.** Interference study of the modified electrode.

**CONCLUSIONS**

Fe-metal oxide has been successfully synthesized in this study. This was proved by visual observation, which has a dark red colour on the surface of the electrode. The electrode can be used as a sensor of oxalate ions. However, the proposed method has the advantages of simple, rapid, and low-cost preparation.

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**REFERENCES**

[1] Crapnell RD, Adarakatti PS, Banks CE. Electroanalytical Overview: The Electroanalytical Detection of Oxalate. Sensors and Actuators Reports [Internet]. 2023;6(July):100176. Available from: https://doi.org/10.1016/j.snr.2023.100176

[2] Zhang K, Zhao Q, Cui D, Gao G, Liu X, Qin A, et al. Enhancing electrochemical lithium-storage properties of hydrated iron oxalate (FeC2O4·2H2O) anode material by combining with dual-state copper. J Alloys Compd. 2024;976(September 2023).

[3] Zhang M, Wang S, Zhong H, Ma X, Cao Z. Spontaneous corrosion on the surface: Ni-regulated oxalates grown in situ on stainless steel for efficient oxygen evolution. J Alloys Compd [Internet]. 2023;968(July):172097. Available from: https://doi.org/10.1016/j.jallcom.2023.172097

[4] Guo Z, Ye C, Shen Y. Effects of electrolyte pHs, temperatures, potentials and oxalate ions on the electrocatalytic reduction of nitrates. J Electroanal Chem [Internet]. 2024;957(February):118143. Available from: https://doi.org/10.1016/j.jelechem.2024.118143

[5] Rana S, Yadav KK, Devi S, Mehta SK, Jha M. Oxalate-mediated synthesis of hybrid nickel cobalt-based nanostructures for boosting water and urea electrooxidation efficiency. J Alloys Compd [Internet]. 2024;990(December 2023):174241. Available from: https://doi.org/10.1016/j.jallcom.2024.174241

[6] Thao VD, Son LT, Lan NT, Huyen MN, Nguyen TT, Le SD, et al. Facile synthesis of mixed nickel-cobalt oxalates with composition control as high-performance electrode materials for supercapacitors. J Energy Storage [Internet]. 2023;66(December 2022):107428. Available from: https://doi.org/10.1016/j.est.2023.107428

[7] Zeng X, Zeng H, Xiong G, Zeng Y, Zhao S, Xiao H, et al. Voltammetry study of CuHCF electrode in brine solutions. Desalin Water Treat [Internet]. 2024;319(June):100533. Available from: https://doi.org/10.1016/j.dwt.2024.100533

[8] Bange AF, Brown GM, Senesac LR, Thundat T. Stripping voltammetry of Pb and Cu using a microcantilever electrode. Surf Sci [Internet]. 2009;603(21):L125–7. Available from: http://dx.doi.org/10.1016/j.susc.2009.09.009

[9] Stankovic D, Roglic G, Mutic J, Andjelkovic I, Markovic M, Manojlovic D. Determination of copper in water by anodic stripping voltammetry using Cu-DPABA-NA/GCE modified electrode. Int J Electrochem Sci [Internet]. 2011;6(11):5617–25. Available from: https://doi.org/10.1016/S1452-3981(23)18432-X

[10] Milhano C, Pletcher D. The electrodeposition and electrocatalytic properties of copper-palladium alloys. J Electroanal Chem. 2008;614(1–2):24–30.

[11] Xu L, Zhang L, Cheng B, Yu J, Al-Ghamdi AA, Wageh S. Significant capacitance enhancement induced by cyclic voltammetry in pine needle-like Ni-Co-Cu multi-component electrode. J Mater Sci Technol [Internet]. 2021;78:100–9. Available from: https://doi.org/10.1016/j.jmst.2020.10.051

[12] Li Sip YY, Fox DW, Shultz LR, Davy M, Chung HS, Antony DX, et al. Cu-Ag Alloy Nanoparticles in Hydrogel Nanofibers for the Catalytic Reduction of Organic Compounds. ACS Appl Nano Mater. 2021;4(6):6045–56.

[13] Comisso N, Cattarin S, Fiameni S, Gerbasi R, Mattarozzi L, Musiani M, et al. Electrodeposition of Cu-Rh alloys and their use as cathodes for nitrate reduction. Electrochem commun [Internet]. 2012;25(1):91–3. Available from: http://dx.doi.org/10.1016/j.elecom.2012.09.026

[14] Suyanta, Sunarto, Padmaningrum RT, Karlinda, Isa IM, Rahadian. Development of voltammetry analysis method of copper metal ions by a solid-state membrane with carbon nanotube. Indones J Chem. 2021;21(2):332–9.

[15] Harsini M, Ayu B, Fitriany E. Chinese Journal of Analytical Chemistry Electrochemical synthesis of polymelamine / gold nanoparticle modified carbon paste electrode as voltammetric sensor of dopamine. 2022;4(June 2021).