

Fabrication and Characterization of Syringe Carbon Paste Electrode for Electrochemical Measurement

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ABSTRACT.

This study aims to fabricate and characterize a syringe carbon paste electrode (SCPE) using $K_3Fe(CN)_6$ 10 mM solution with cyclic voltammetry technique. Characterization is performed by varying pH (pH 4, 7, and 10) and scan rate (30 - 100 mV/s) so that the characteristics of SCPE can be observed. The $K_3Fe(CN)_6$ 10 mM solution test results at various pH variations obtained the largest anodic peak current (I_{pa}) at pH 10 was 44.75 μA . The scan rate results at various pH showed linear results with the diffusion coefficient of $1.77 \times 10^{-6} \text{ cm}^2/\text{s}$, $1.65 \times 10^{-6} \text{ cm}^2/\text{s}$, and $2.50 \times 10^{-6} \text{ cm}^2/\text{s}$ with r values of 0.9994, 0.9975, and 0.9992 for pH 4, pH 7, and pH 10 respectively. This indicated that a diffusion process controlled this system's mass transfer in various pH. The detection of nitrite ions at a concentration of 2 mM showed a clear oxidation peak, with the highest I_{pa} value of 61.28 μA in pH 7 buffer solution.

Keywords: characterization, cyclic voltammetry, $K_3Fe(CN)_6$, syringe carbon paste electrode

1. INTRODUCTION

Electrochemical measurement has undergone significant advancements with the development of versatile, cost-effective, and sensitive electrodes that can be fabricated with simple procedures [1]. Among various electrode materials, the carbon paste electrode (CPE) has emerged as an effective tool due to its advantageous properties, such as ease of fabrication, tunable surface chemistry, and high conductivity [2]. Carbon paste electrodes, composed of a mixture of carbon particles and a binder (often a non-conductive oil or polymer), are particularly useful for applications requiring rapid and sensitive detection of electroactive species. The flexibility of CPEs lies not only in their low cost and ease of preparation but also in their ability to be modified with a wide range of materials to enhance their electrocatalytic properties [3][4]. This allows for customization in applications ranging from environmental monitoring to biological sensing

[5][6][7]. In this context, the syringe carbon paste electrode (SCPE) represents a promising modification of the traditional CPE, allowing for better control over the electrode's size, surface area, and reproducibility [8][9].

The syringe carbon paste electrode is fabricated using a simple syringe as the primary body, which serves as the housing for the carbon paste. This approach is advantageous as it allows for easy handling, uniform distribution of the carbon paste, and the ability to control the electrode dimensions with high precision. The fabrication process generally involves filling the syringe with a homogeneous mixture of carbon powder and binder and then packing the mixture to form a compact, conductive surface at the end of the syringe barrel [10]. The unique design of the SCPE also allows for periodic renewal of the electrode surface by extruding a small portion of the carbon paste, thereby exposing a fresh, uncontaminated surface for each

measurement. This feature is particularly beneficial in analytical applications where electrode fouling is a common issue, as it ensures consistent electrochemical responses without the need for complicated cleaning procedures [11].

Characterization of the SCPE involves assessing its electrochemical behavior, typically performed through techniques such as cyclic voltammetry (CV). Cyclic voltammetry is useful for determining the reversibility and stability of redox reactions occurring on the electrode surface [12][13]. The ability to customize the composition of the carbon paste also allows for the incorporation of functional groups or nanomaterials that can further enhance the electrode's electrocatalytic properties. For instance, introducing metal nanoparticles [9][14], polymers [15][16], or carbon nanostructures can significantly improve the sensitivity and selectivity of the SCPE for specific analytes [17][18].

The SCPE holds promise for many applications due to its adaptability, cost-efficiency, and ease of use. Furthermore, the electrode's renewable surface is ideal for real-time and on-site analysis, making it suitable for point-of-care applications where quick and accurate results are essential. In this study, we present the fabrication and characterization of a SCPE for the electrochemical detection of nitrite ions using CV and Linear Sweep Voltammetry (LSV) techniques. Variations in pH and scan rate will also be carried out to enhance information on the electrochemical behavior of SCPE.

2. METHODS

In this study, the polyethylene syringe was modified by cutting the tip of an electrode so a 1 mm muzzle with an inner diameter of 2 mm was left, and the plunger was modified so that a copper wire could be inserted. The copper wire can be in contact with carbon paste on the inside of the syringe. The CV technique characterized the syringe carbon paste electrode by varying the scanning rate and pH. In addition, tests were carried out to detect nitrite ions at different pH values using LSV.

2.1. Materials and Tools

The materials used in this research are graphite powder, a modified syringe, buffer pH 4, buffer pH 7, buffer pH 10, paraffin oil, and distilled water. The solutions tested in this study were $K_3Fe(CN)_6$ 10 mM. The tools used in this research are an eDAQ-Potentiostat with a three-electrode system, a syringe carbon paste electrode (SCPE), a Pt electrode, an Ag/AgCl electrode, and a polyethylene container.

2.2. Experiment

2.2.1. Fabrication of syringe carbon paste electrode

Syringe carbon paste electrode development is done by mixing graphite powder and paraffin oil into a mortar in a ratio of 7:3 and then stirring until homogeneous. The paste formed is put into a syringe and compressed with a plunger until a small quantity of carbon paste comes out of the tip of the syringe. The carbon paste that came out of the syringe tip was cleaned using filter paper and flattened so that the surface of the contact area had a diameter of 2 mm. The syringe carbon paste electrode was dried for 24 hours at ambient temperature to optimize the binding process and can then be used for measurements.

2.2.2. Electrochemical performance of syringe carbon paste electrode

Cyclic voltammetry (eDAQ-Potentiostat) with three system electrodes was used to evaluate the electrochemical performance of the syringe carbon paste electrode. The electrodes consist of the syringe carbon paste electrode, Ag/AgCl, and Pt as working, reference, and counter electrodes. The Potential range was set from -0.5 V to +1.0 V with $K_3Fe(CN)_6$ 10 mM in several pH conditions as an electrolyte. Furthermore, mass transport analysis was conducted by varying the scanning rate from 30 to 100 mV/s.

3. RESULTS AND DISCUSSION

3.1. Fabrication of syringe carbon paste electrode

Figure 1 illustrates a detailed schematic diagram of the carbon paste electrode, highlighting its composition and structure. Paraffin is a binder in this

design, maintaining the electrode material's mechanical stability and integrity.

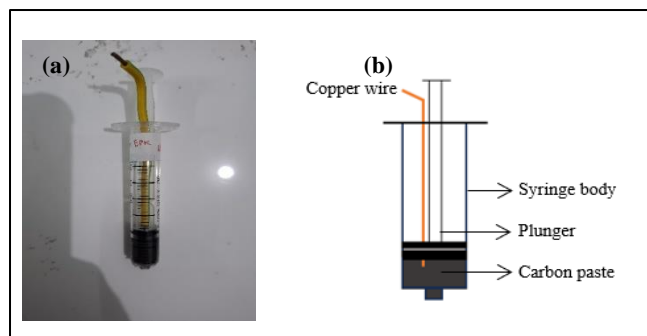


Figure 1. (a) Photo of 3 mL syringe carbon paste electrode; (b) schematic representation of syringe carbon paste electrode.

3.2. Electrochemical study of syringe carbon paste electrode

Electrochemical sensitivity and electron transfer rate of the syringe carbon paste electrode were investigated using cyclic voltammetry at a range potential from -0.5 V to +1.0 V using a $K_3Fe(CN)_6$ electrolyte system in several pH conditions. Figure 2 and Table 1 show that the anodic peak response for pH 4, 7, and 10 was 26.68 mV, 36.76 mV, and 44.75 mV, respectively.

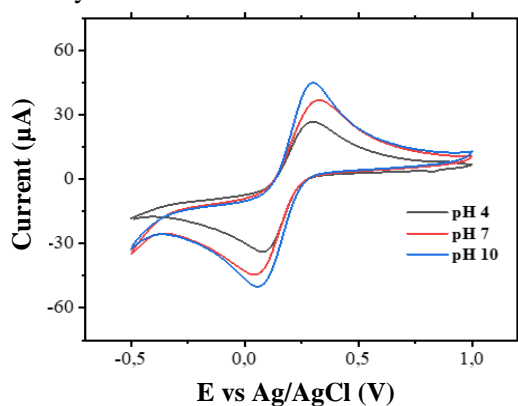


Figure 2. Syringe carbon paste electrode cyclic voltammogram of $K_3Fe(CN)_6$ 10 mM in various pH solutions.

The anodic current response was increased when the pH solution changed to alkaline. The higher anodic current response indicated that the syringe carbon paste electrode was sensitive. The phenomenon occurs due to the amount of ion OH^- abundant in higher

pH, which leads to better conductivity of the electrolyte and higher current response [19]. Besides, the separation between the anodic and cathodic peaks in alkaline conditions was 0.234 mV, calculated using Equation (1).

$$\Delta E = E_{pa} - E_{pc} \quad (1)$$

E_{pa} and E_{pc} are potential anodic and cathodic peaks, respectively. The ΔE value was smaller than the neutral condition and not much different from the acidic condition. It indicated that alkaline conditions provide a faster electron transfer rate.

Table 1. Current of oxidation-reduction peak (I_{pa} - I_{pc}) and potential (E_{pa} - E_{pc}) of $K_3Fe(CN)_6$ in various pH conditions.

Parameters	CPE pH Variation		
	pH 4	pH 7	pH 10
I_{pa} (μA)	26.68	36.76	44.75
I_{pc} (μA)	-33.66	-44.45	-50.06
E_{pa} (V)	0.294	0.322	0.296
E_{pc} (V)	0.088	0.048	0.062
ΔE (V)	0.206	0.274	0.234

Mass transport was evaluated using a $K_3Fe(CN)_6$ redox system with scan rate variation from 30 mV/s to 100 mV/s. Figure 3 denoted the increasing current response directly proportional to the scan rate. When the scan rate increases, the diffusion layer becomes thinner, which results in a higher current response. The linear plot between the current anodic response (I_{pa}) and the square root of the scan rate (\sqrt{v}) showed linearity for each pH condition, as shown in Figure 4.

This indicated that the mass transfer in this system was mainly controlled by the diffusion process with the diffusion coefficient of $1.77 \times 10^{-6} \text{ cm}^2/\text{s}$, $1.65 \times 10^{-6} \text{ cm}^2/\text{s}$, and $2.50 \times 10^{-6} \text{ cm}^2/\text{s}$ with a correlation coefficient value of 0.9994, 0.9975, and 0.9992 for pH 4, pH 7, and pH 10 respectively (Table 2). The peak

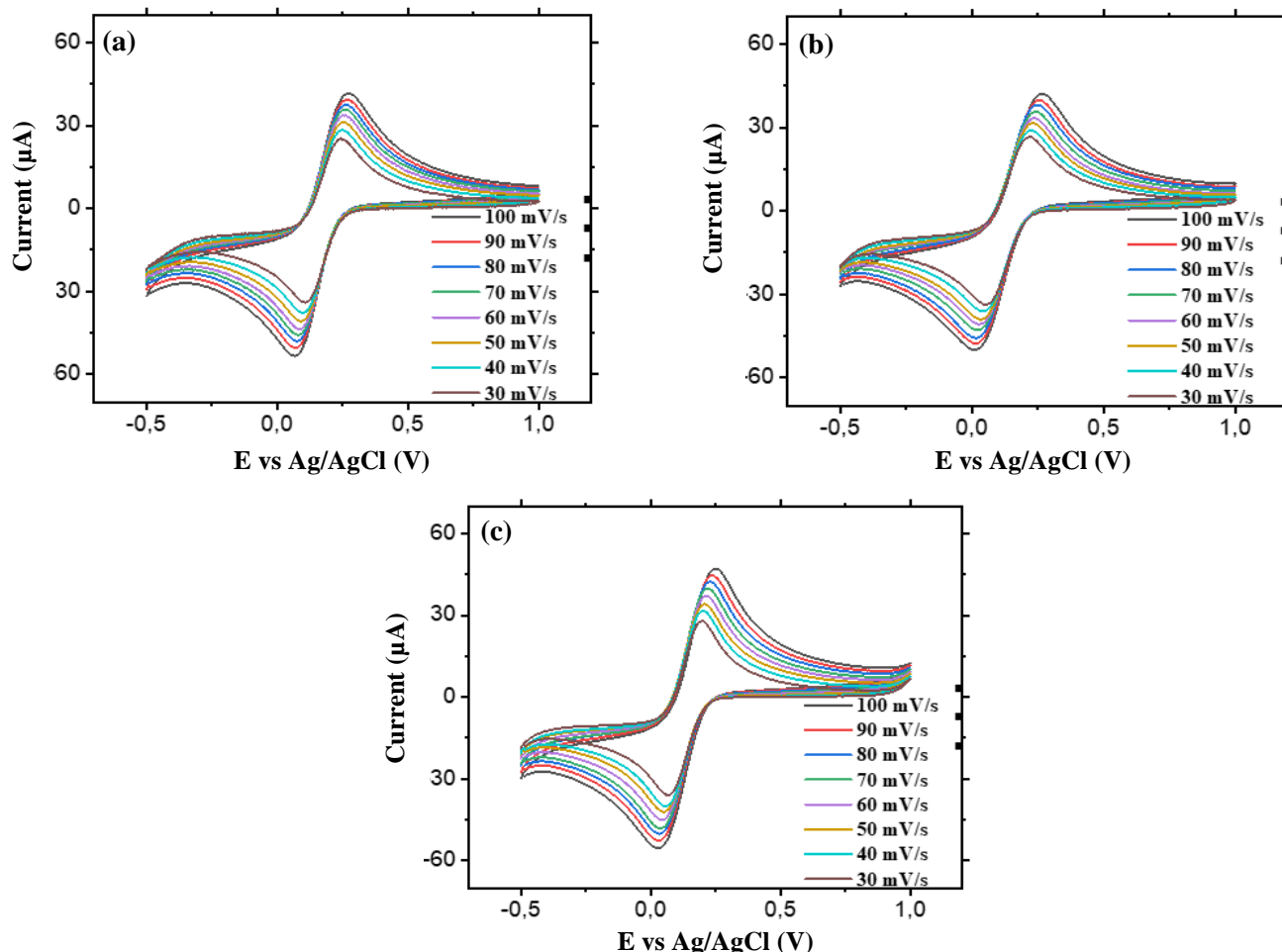


Figure 3. Cyclic voltammogram of $K_3Fe(CN)_6$ at various pH and scan rates. (a) pH 4, (b) pH 7, and (c) pH 10.

current of a quasi-reversible system, which is controlled by the diffusion process, was calculated by using The Randles-Sevcik equation (2)

$$i_p = (2.69 \times 10^5) n^{3/2} AD^{1/2} \nu^{1/2} C_A \quad (2)$$

where n is the number of electrons involved in the redox reaction, A is the cross-sectional area of the working electrode (0.0314 cm^2), D is the diffusion coefficient for the electroactive species, ν is the scan rate, and C_A is the concentration of the electroactive species at the electrode ($1.0 \times 10^{-5} \text{ mol/cm}^3$). The Diffusion coefficient (D) is one of the fundamental properties of a redox-active compound. When considered from its value, pH 10 has the most significant diffusion coefficient and can be related to the conductivity properties of this system. This possibility is what causes the increase in anodic peak current (I_p) in pH 10 [19].

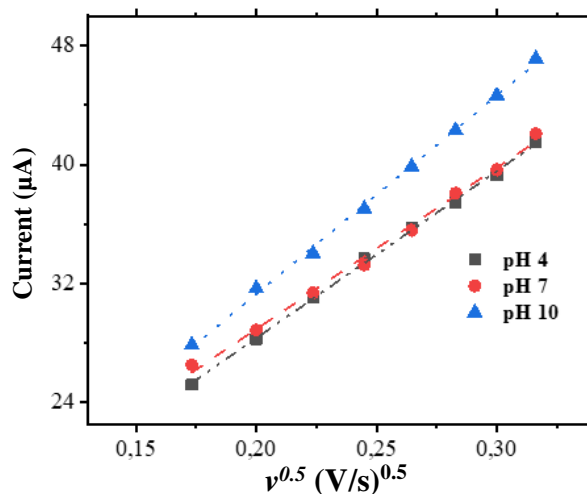


Figure 4. The plot of Randles-Sevcik equation with various pH

Table 2. Diffusion coefficient (D) value for each pH variation with correlation coefficient and regression equation.

pH Variation	Regression Equation	Correlation Coefficient (r)	Diffusion Coefficient (cm ² /s)
pH 4	$y = 0,000112x + 0,000006$	0,9994	$1,77 \times 10^{-6}$
pH 7	$y = 0,000108x + 0,000007$	0,9975	$1,65 \times 10^{-6}$
pH 10	$y = 0,000133x + 0,000005$	0,9992	$2,50 \times 10^{-6}$

3.3. Nitrite Ion Detection

A syringe carbon paste electrode was employed to detect nitrite ions using the linear sweep voltammetry technique with various pH, and the result is presented in Figure 5. pH has an essential role in detecting nitrite ions. An anodic oxidation peak was obtained at a range potential from 0.920 V to 0.922 V. The anodic current response differed for each pH variation, and the highest oxidation peak was obtained in the measurement of nitrite ions in a pH 7 solution with a peak current of 61.28 μ A. This result is appropriate with previous work [20]. The anodic current response is low at pH = 4 due to the large amount of NO₂ ions tending to be protonated under strongly acidic conditions and unstable electroactive species from HNO₂ (pKa HNO₂ = 3.3 at 25 °C). Besides, NO₂ ions undergo a disproportionation reaction in strongly acidic solutions. When pH > 7, an oxide layer forms on the electrode surface, inhibiting the oxidation of nitrite ions [21]. The amount of hydrogen ions decreased, leading to a declining anodic current response. However, the shape of the oxidation peak remains relatively stable when pH is varied, as shown in Figure 5.

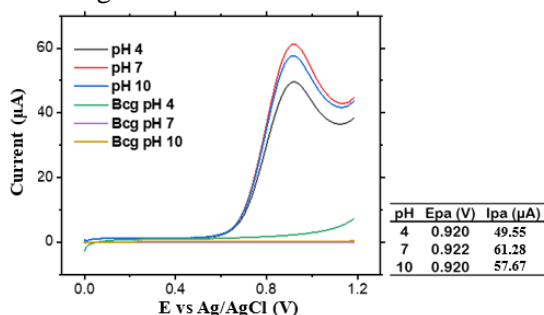


Figure 5. Linear sweep voltammogram of nitrite ions in various pH with the background (Bcg) of each pH solution absent of nitrite ions.

4. CONCLUSION

Fabrication and characterization of SCPE using K₃Fe(CN)₆ 10 mM solution showed the highest oxidation-reduction peak in pH 10. The mass transfer was controlled by a diffusion process, with the highest diffusion coefficient being $2,50 \times 10^{-6}$ cm²/s. Detection of nitrite ion at a concentration of 2 mM showed a clearly defined oxidation peak with the highest peak at pH = 7. The change in pH only affects the oxidation current peak, while the shape of the oxidation peak tends to be stable. Thus, SCPE performed well and can be used for electrochemical detection in aquatic matrix.

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