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Research Article

Development of modified polyaniline-pencil graphite electrode (PANI/PGE) as a corrosion electrochemical sensor for the voltammetric detection of Fe^{2+} ions

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Abstract

This study has developed a pencil graphite electrode (PGE), modified with polyaniline (PANI), to serve as a simple, selective, and sensitive electrochemical sensor for the voltammetric detection of Fe^{2+} ions, specifically for quantifying iron in corrosion studies. The modification of PANI on the PGE (PANI/PGE) was performed through electropolymerization process by cyclic voltammetry (CV) in a potential range of –1 V to 1 V at a scan rate of 100 mV/s for 20 cycles. The active surface area was calculated to increased by 35% upon the modification. The CV and potentiodynamic polarization were utilized to study the anodic behaviour of the Fe^{2+} ions. The PANI/PGE exhibited good electrocatalytic activity and significantly enhanced peak current ratio of approximately 1.83 compared to the bare PGE, making it effective for determining the corrosion rate of mild steel. Parameters including electroactive surface area, the effect of scan rate, and sensitivity were investigated. The cyclic voltammogram of the PANI/PGE showed a good linearity in the concentration range 0.005 M to 0.05 M with the detection limit of of 1×10^{-2} M and quantification limit of 3×10^{-2} M. Notably, the PANI/PGE electrode demonstrated a higher detection of Fe^{2+} ions compared to the bare PGE electrode. Specifically, at 7 days, the current for the PANI/PGE electrode increased by 48%, while at 35 days, it increased by 32%, highlighting the enhanced performance of the modified electrode. The development of the modified PGE as an electrochemical sensor for detecting corrosion in mild steel has been successfully achieved. This study underscores the enhanced sensitivity and selectivity of the PANI-modified PGE, showcasing its potential for efficient on-site detection by quantifying Fe^{2+} ions in corrosion samples.

Keywords: mild steel; cyclic voltammetry; electrochemical sensor; pencil graphite electrode

Introduction

Corrosion in metallic structures is a pervasive global issue that significantly impacts various industrial applications [1]. This destructive process arises from a thermodynamic electrochemical reaction between a metal and chemical species in its environment, leading to the deterioration of the metal's physical and chemical properties [2]. Such degradation can weaken the structural integrity of metals, resulting in substantial economic losses and compromised product quality, especially in industries reliant on metallic equipment [3]. Early detection of corrosion is crucial for maintaining metal structures, extending their service life, and preventing accidents. Various sensors have been developed to monitor parameters related to corrosion. Conventional techniques such as thermal imaging, ultrasonic testing, radiographic methods, electrochemical analysis, and electromagnetic methods, although effective, are often labor-intensive, time-consuming, and costly [4]. In recent years, researchers have focused on developing smart corrosion detectors as more convenient alternatives [5,6]. Given the demand for rapid and simple sensors to detect corrosion in mild steel, which is an alloy primarily composed of iron and extensively used in numerous industrial sectors, pencil graphite electrodes (PGEs) have emerged as a favorable material. PGEs are easy to modify, commercially available, low-cost, disposable, and exhibit high electrochemical reactivity. They have been widely used in electroanalytical applications, often preferred over other carbon electrodes due to their lower background currents, higher sensitivity, and good reproducibility [7]. To enhance the properties of PGEs, modifications such as coating with conductive polymers like polyaniline (PANI) are employed. These modifications improve the electrode's working potential range, selectivity, and sensitivity [8-10]. Conductive polymers offer flexibility, stability, and enhanced conductivity, making them ideal for achieving the desired sensor performance [11]. The combination of PGEs and conductive polymers has been extensively studied, resulting in electrochemical sensors with higher sensitivity and ease of handling [12], for various targeted analytes. For instances, Selvaraj et al. reported the modification of PGEs with polymeric hydrogels based on acrylamide and 2-acrylamido-2-methylpropane sulfonic acid, copolymerized with aniline and pyrrole, for the detection of methylene blue [11]. Their study demonstrated significant improvements in sensing behavior due to the copolymerization of aniline and pyrrole with the hydrogel. Yaacob et al. highlighted the enhanced sensitivity of PGEs modified with functional monomer polypyrrole for sensing ascorbic acid [13]. Additionally, Özcan et al. reported that PGEs modified with poly(pyrrole-3-carboxylic acid) exhibited a synergistic effect and were capable of selectively detecting dopamine in the presence of common interferents [14]. A recent study by Goldoni et al. demonstrated the fabrication of a molecularly imprinted PANI layer on pencil graphite electrodes (PGEs) using an in situ electrosynthesis method for the impedimetric detection of chloramphenicol, a pharmaceutical residue [15]. The process involved the dimerization of electro-oxidized aniline moieties, leading to the formation of the emeraldine base. Further redox transitions produced the redox-active pernigraniline form, which contributed to the reversible behavior of the film. This redox activity enhanced the conductivity of the PANI layer, resulting in greater sensitivity and a stronger current response in the detection process. In addition to pharmaceutical residue detection, the application of PANI-based electrodes has been extended to the monitoring of heavy metal ions. In 2024, Wu et al. reported the development of a PANI-based nanocomposite electrode for the sensitive detection of Cd^{2+} ions in wastewater using differential pulse anodic stripping voltammetry (DPASV) [9]. The enhanced electrochemical response was attributed to the synergistic effect between the highly conductive PANI chains and embedded ultrafine gold nanoparticles (AuNPs), which provided a high density of electroactive surface atoms. Moreover, the PANI matrix offered functional groups such as imine and amine, which facilitated coordination bonding with electron-deficient Cd(II) ions via electron donation. In similar year, Maheshwaran et al. reported a PANI-quinoxaline based electrode for detection of Hg^{2+} and Pb^{2+} ions via differential pulse voltammetry (DPV) [16]. The enhanced performance of the sensor was attributed to the reduced band gap energy of the modified polymer, which facilitated improved charge transfer and resulted in higher sensitivity towards heavy metal ions.

On-site detection in the industry is often limited, complicating and delaying the detection of corrosion in mild steel. Significant time is required to collect samples and conduct analyses in the laboratory [17]. For example, in industries such as oil and gas, where corrosion occurs beneath insulation materials, detecting corrosion under insulation (CUI) is difficult because it is hidden, and traditional methods like visual inspection are often insufficient. Techniques such as neutron backscatter, capacitive imaging, and pulsed eddy current are used, but they have limitations in terms of accuracy and cost [18]. The U.S. Environmental Protection Agency (EPA) also outlines methods for testing the corrosivity of liquid wastes toward steel [19]. These methods involve exposing steel coupons to waste and measuring the degree of corrosion. The process is detailed and requires precise control of experimental conditions, making it labor-intensive and time-consuming. Therefore, the development of PGEs that can be mobilized to the site is crucial. This advancement can significantly reduce the time required for detection and enable early identification of corrosion. Consequently, it helps maintain metal equipment in optimal condition and prevents potential accidents.

The modification of the electrode in this study aims to enhance the electrical conductivity of the PGE. Although PGEs are already recognized as excellent materials for sensors, modifying them with conductive polymers such as polyaniline (PANI) has demonstrated improved performance in detecting corrosion in mild steel. The PGE was created using mechanical pencil lead and modified with PANI through an electropolymerization process using cyclic voltammetry (CV) technique. An Fe^{2+} ion calibration curve was established as standard curves using both the PGE and the PANI-modified PGE to compare their sensitivity and quantify the corrosion products. The corrosion rate was calculated from the cyclic voltammogram data, with observations conducted from day 7 to day 35. This study highlights the improved sensitivity and selectivity of the PANI-modified PGE, demonstrating its potential for efficient on-site corrosion detection in mild steel.

Materials and Methods

Materials

The chemicals and reagents used in this study were commercially sourced and of analytical grade, used without further purification. Copper wire, steel sheets, aniline, hydrochloric acid, epoxy resin, araldite, potassium ferricyanide, potassium nitrate, iron(II) sulphate, sodium chloride were purchased from Sigma Aldrich (USA), J.T. Baker (USA), Merck (Germany) and QRec (Malaysia), respectively. Pencil graphite leads from brand BUNCHO of 0.7 mm diameter and length of 60 mm were used.

Instruments

The polyaniline sample was characterized using Fourier Transform Infrared (FTIR) spectroscopy in direct transmittance mode, employing a Perkin Elmer System 2000 spectrometer (Waltham, MA, USA). KBr pellets were prepared in a 1:20 (w/w) ratio for this analysis. The spectra were observed at region between 4000 cm^{-1} to 400 cm^{-1} with a resolution of 4 cm^{-1} and 32 scans per sample. All the electrochemical measurements were carried out using an electrochemical workstation named Wheestat Potentiostat that had been using three electrode systems. Platinum wire and saturated calomel were used as a counter electrode (CE) and reference electrode (RE) respectively while PGE has been used as a working electrode (WE).

Development of unmodified and modified pencil graphite electrode

The mechanical pencil lead with 0.7 mm diameter and 60 mm length was used to develop PGE for the study of Fe ions. The pencil lead was coiled with copper wire at one end for the electrical contact. Then it will be inserted into the empty syringe containing the araldite mixture where it has a ratio of epoxy resin of 1:1. After 24 h of drying, the tip of the PGE was renewed by using a sharp blade and then smoothened by sand paper for a better conduction. Subsequently, the bare pencil graphite electrode was modified with polyaniline (PANI) via an electropolymerization process utilizing the cyclic voltammetry (CV) technique. Initially, 0.1 M aniline was dissolved in 1 M of 37% (w/w) hydrochloric acid (HCl) solution [20] and oxidized with nitrogen (N_2) gas for 10 minutes. This mixed solution was then electropolymerized by CV at a scan rate of 100 mV/s for 20 cycles. Following the completion of the polymerization process, the resulting dark green polyaniline powder was obtained through filtration and thoroughly washed with distilled water. The dark green powder was then dried in the oven at 50 °C for 24 h.

Electrochemical measurements by cyclic voltammetry (CV)

Determination of electroactive surface area

An electrolyte solution consisting of 2 mM $K_3[Fe(CN)_6]$ and 1 M KNO_3 in 100 mL of distilled water was prepared. The solution was then purged with nitrogen gas (N_2) for 10 minutes for oxygen removal. The cyclic voltammograms of $[Fe(CN)_6]^{3-}$ were acquired at different scan rates. The electroactive surface area of the bare and modified electrode was calculated by using the Randles-Sevick equation:

$$Ip = 2.69 \times 10^5 n^{3/2} A D_o^{1/2} C_o^* v^{1/2} \qquad \text{(Eq. 1)}$$

Where Ip is peak current (microampere) specifically the anodic peak current (Ipa) in this study, n indicates the number of electron transferred where n=1 for $K_3[Fe (CN)_6]$, A is the surface area of the electrode (cm^2), D_o is the diffusion coefficient that is obtained from the slope of the graph by plotting Ipa vs. $v^{1/2}$, C_o^* is the concentration of electroactive species (mol cm^{-3}), and v is the scan rate (Vs^{-1}).

Preparation of Fe^{2+} standard calibration curve

A 500 mL Fe^{2+} standard solution was prepared by dissolving 3.5% (w/v) NaCl and 99.5% (w/w) $FeSO_4$ in distilled water, to replicate chloride-rich conditions typical of corrosion environments (pH~4).This solution was subsequently diluted to 10 different concentrations: 0.005, 0.01, 0.015, 0.02, 0.025, 0.03, 0.035, 0.04, 0.045 and 0.05 M in 50 mL of volumetric flasks. Prior to analysis, each solution was purged with N_2 gas and then subjected to the CV process. The peak current for each concentration was recorded at a scan rate of 100 mV/s. A calibration curve was custructed by plotting the anodic peak current (Ipa) against the corresponding concentrations.

Determination of sample solution concentration

Each mild steel sheets were cut with dimension 3 cm x 3 cm and polished with sand paper until the surface was smooth. All the mild steel sheets were then immersed in 100 mL of 3.5% (w/v) NaCl solution in 5 different beakers according to their respective days. The observation period extended over 7, 14, 21, 28, and 35 days. At each interval, the mild steel sheet was removed from the solution, which was then filtered. The filtrate was purged with N_2 gas and subsequently analyzed using CV technique to determine its Ipa. This procedure was repeated for samples collected on the 14th, 21st, 28th, and 35th days. The concentration of the sample solution was determined by the calibration curve plotted in the *Preparation of Fe^{2+} Standard Calibration Curve* section.

Determination of corrosion rate

The corrosion rate was calculated using the following equation:

Corrosion rate (mmpy) = mass of dissolved Fe/ (area x times x density of Fe) (Eq. 2)

Results and Discussion

Modification of bare PGE

Polymerization of aniline by cyclic voltammetry (CV)

Fig. 1 depicts the voltammogram of polyaniline polymerization on the bare PGE. Oxidation and reduction peaks were observed at 0.132 V and 0.303 V, respectively, during the first cycle. The produced current increased after each cycle, indicating an increase in the deposition rate. However, a shifting in potential was observed, suggesting hindrances in the redox processes. This phenomenon could be attributed to the deposition of PANI, which subsequently covered the electrode surface. This coverage disrupted the electron transfer between the redox-active species and the electrode, despite the high sensitivity properties created. A similar phenomenon was reported by Goldoni et al., where the formation of pernigraniline, a fully oxidized form of PANI composed predominantly of quinoid units occurred around +0.45 V. This redox process involves the transfer of one electron and two protons and is generally associated with a decrease in conductivity. This observation aligns well with the cyclic voltammetry (CV) behavior in this study, where a gradual anodic peak shift toward ~0.5 V was recorded by the 20th cycle, suggesting the onset of overoxidation and a transition toward the less conductive pernigraniline state [15]. **Fig. S1** illustrates the mechanism of PANI polymerization, which includes four main steps: (1) formation of a primary cation-radical, (2) formation of dimers through deprotonation and re-aromatization, (3) further growth and chain formation with oxidation and (4) spontaneous doping of the resulting polymeric chain to obtain the polymer in the doped form. The structure of PANI formed at the end of the process consists of two repeating units: quinoid rings and benzene rings [20].

Charaterization of polyaniline (PANI)

The FTIR spectrum of electropolymerized polyaniline (PANI) is shown in **Fig. 2**. The spectrum exhibits a distinct peak at 1056 cm^{-1}, which is attributable to the medium absorption of C-N bond vibrations in benzoic rings [21]. Additionally, the distinctive peaks seen at 1165 cm^{-1} and 1375 cm^{-1} can be assigned to the vibrations of the C-N group in similar rings [22]. The absorption peak observed at 1639 cm^{-1} can be attributed to the stretching vibrations of quinoid rings in PANI [23]. This is followed by a sharp peak at 1433 cm^{-1}, corresponding to the C=C stretching of benzenoid rings, which is in agreement with previously reported values, such as those described by Ajeel et al. [24]. These two bands, associated with the quinoid and benzenoid rings, have been widely used to assess the degree of oxidation of PANI. The variation in their relative intensities reflects the oxidation process, where benzenoid rings are gradually converted into quinoid rings, followed by the oxidation of amino groups into imino groups within the polymer backbone [25]. At higher frequencies, a distinct peak is observed at 2898 cm^{-1}, corresponding to C–H bond vibrations, while a broader peak at 3343 cm^{-1} is attributed to N–H bond vibrations. In addition, consistent with the findings reported by Qin et al., the stretching vibration at 1056 cm^{-1} can be attributed to protonated PANI, while the appearance of a band around 1114 cm^{-1} is associated with the deprotonation process, indicating the transformation of the emeraldine form into pernigraniline [26]. Emeraldine is the partially oxidized and electrically conductive form of polyaniline, characterized by a balanced presence of benzenoid and quinoid structures. The detection of both these signals in the FTIR spectrum suggests that such redox transitions occurred during the electrosynthesis process, which may influence the electrochemical behavior of the PANI film.

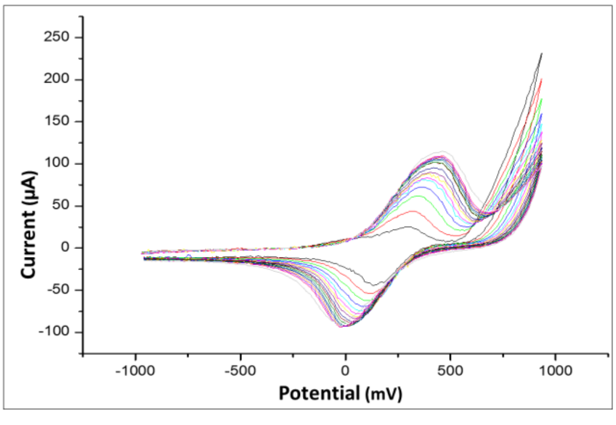

Figure 1. Cyclic voltammogram of polyaniline (PANI) polymerization for 20 cycles

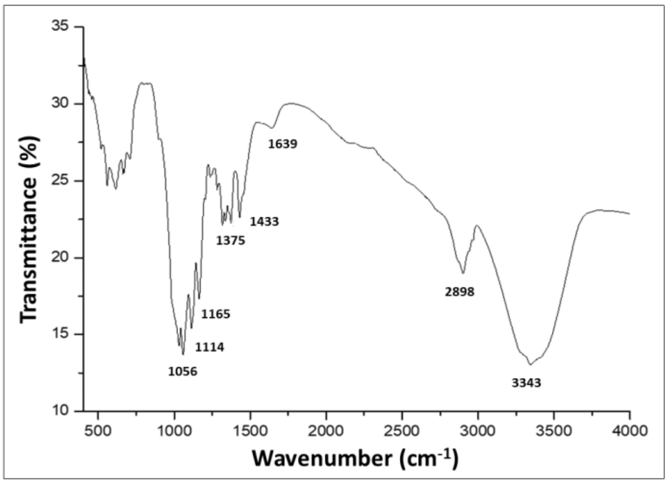

Figure 2. FTIR spectrum of electropolymerized polyaniline (PANI)

Electroactive surface area of bare and modified PGE

Fig. S2. shows the cyclic voltammogram of [Fe $(CN)_6]^{3-/4-}$ by PGE (curve A) and modified PGE with PANI (curve B). A noticeable increase in Ipa was observed in the voltammogram of PANI/PGE compared to the bare PGE. This increase in peak current at the modified PGE can be attributed to the higher rate of electron transfer facilitated by the conductive and electrocatalytic properties of PANI. PANI's redox-active sites generally participate in electron transfer reactions, acting as mediators that enhance the electrocatalytic activity of the electrode [27,28]. Additionally, the increase in the electroactive surface area, caused by more reductive and reverse oxidation processes of ferricyanide ions, contributed to the overall enhancement [29]. The redox reaction of [Fe $(CN)_6]^{3-/4-}$ are shown in the equation below:

Reduction: $Fe(CN)_6^{3-} + e^- \rightarrow Fe(CN)_6^{4-}$ (Eq. 3)

Oxidation: $Fe(CN)_6^{4-} \rightarrow Fe(CN)_6^{3-} + e^-$ (Eq. 4)

The electroactive surface area for both bare PGE and modified PGE was investigated using the electrochemical reaction of the [Fe $(CN)_6]^{3-/4-}$ redox system in the presence of KNO_3 as a supporting electrolyte. This setup inhibits the migration of electroactive species in the electric field gradient, resulting in a smooth and uninterrupted redox reaction across different scan rates, as measured by the CV technique. The values were calculated by substituting the data in Randles-Sevick equation, as shown in the electroactive surface area determination. The active surface areas of the bare PGE and PANI/PGE are 3.8684 cm^2 and 5.2458 cm^2, respectively.

Calibration curve of Fe^{2+} Standard Solution

The cyclic voltammogram of $FeSO_4$ at different concentrations displayed an anodic peak at 840 mV for the bare PGE (**Fig. 3(A)**) and at 844.5 mV for the PANI-modified PGE (**Fig. 3(B)**), indicating a slight shift in potential due to the modification. The intensity of the Ipa for the PANI-modified PGE was also higher compared to the bare PGE, resulting from the increased number of active sites available for the electrochemical process. Two linear graphs of current (Ipa) against concentration (M) are plotted for the bare PGE (**Fig. 3(C)**) and the PANI/PGE (**Fig. 3(D)**) over a concentration range of 0.005 M to 0.05 M of 99.5% $FeSO_4$.

The linear equation acquired for bare PGE and PANI/PGE are: Ipa (μA) = 2582.53048 (M) – 2.4392 (R^2 = 0.9946) and Ipa (μA) = 5003.76268 (M) + 10.5646 (R^2 = 0.9919), respectively. The respective values of the limit of detection (LOD) and limit of quantification (LOQ) for the PANI/PGE were calculated to be 1×10^{-2} M and 3×10^{-2} M, using the formulas: LOD = 3×SD/b and LOQ = 10×SD/b, where SD is the standard deviation of the intercept and b is the slope of the calibration plot [30]. The modified PGE with PANI exhibited a lower LOD, indicating higher sensitivity towards Fe^{2+} as it can detect the electrochemical activity at an aqeduate concentrations.

Table 1 represents the electrodynamic data including peak-to-peak separation (ΔE_p) and peak current ratio (Ipa/Ipc) of the modified electrodes. The ΔE_p for the bare PGE was measured to be approximately 800 mV, while the PANI-modified PGE exhibited a larger ΔE_p of about 1000 mV. In a reversible redox system, such as Fe^{2+}/Fe^{3+}, the theoretical ΔE_p is typically around 59 mV at room temperature, indicating fast electron transfer kinetics. The significantly higher ΔE_p values observed here suggest quasi-reversible or irreversible behavior at both electrodes, implying slower electron transfer rates. The increased ΔE_p for the PANI-modified electrode compared to the bare PGE might

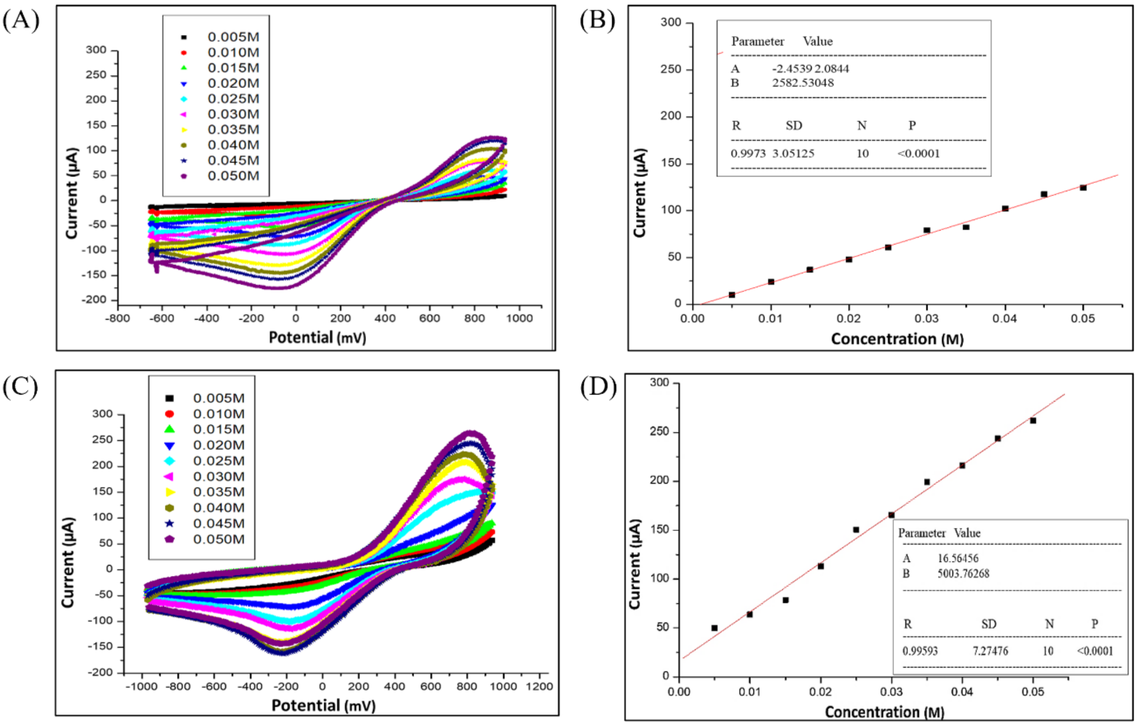

Figure 3. Cyclic voltammogram for standard $FeSO_4$ solution using (A) bare PGE; (B) PANI/PGE and the linear graph of anodic peak current (Ipa) vs concentration (M) for (C) bare PGE and (D) PANI/PGE

be attributed by its morphological structure. While the PANI layer enhances overall electron transfer through its conductive polymer network, it may introduce additional resistance or impair charge transfer kinetics due to the polymer's thickness, or interaction with the Fe^{2+} species. Moreover, the PANI film may cause changes in the electrochemical environment at the electrode surface, such as hindered diffusion or altered double-layer capacitance, contributing to the larger ΔE_p. Ideally, the Ipa/Ipc ratio should be close to 1 in a reversible redox system, such as the Fe^{2+}/Fe^{3+} couple, indicating symmetric oxidation and reduction behavior. In this study, the bare PGE electrode exhibited ratio of 0.71 when tested with Fe^{2+}, suggesting inefficient electron transfer and limited redox reversibility. This may be attributed to surface resistance or the lack of active sites on the unmodified electrode. In contrast, the PANI-modified PGE demonstrated a significantly improved ratio of 1.83, reflecting enhanced oxidation current of Fe^{2+} to Fe^{3+}. The conductive and electroactive nature of polyaniline likely facilitated efficient charge transfer. However, the ratio's deviation from unity indicates that the redox process is quasi-reversible, potentially influenced by surface interactions or slower reduction kinetics at the modified interface.

Table 2 displayed reported works related to the utilization of PGE and PANI-based electrodes for electrochemical detection of Fe^{2+}/Fe^{3+}. Based on the comparison study, although the PANI/PGE sensor exhibits a higher detection limit ($\sim 1 \times 10^{-2}$ M) compared to other PANI-based platforms designed for trace Fe^{2+} detection, it remains highly effective for corrosion monitoring. This is primarily due to corrosion processes typically release Fe^{2+} in relatively high concentrations, well within the sensor's detection range. Importantly, unlike the previously reported studies that focus on trace detection or speciation of Fe^{2+}/Fe^{3+} in water samples, no reported work has combined PANI-modified PGEs specifically for the purpose of monitoring Fe^{2+} released from corroding metal substrates. This highlights the novelty and application-specific relevance of the present sensor design. The demonstrated performance in detecting Fe^{2+} from real corroded steel further validates its effectiveness and robustness, supporting its use in practical corrosion studies.

Fig. 4(A) and and **4(B)** present the cyclic voltammograms of the sample solution from the 7th day to the 35th day for bare PGE and modified PANI/PGE, respectively. Both voltammograms displayed a consistent trend; the longer the mild steel was immersed, the higher the anodic peak current, indicating an increased redox reaction process of Fe^{2+} ions. Notably, the voltammogram of bare PGE (**Fig. 4(A)**) showed a distinct potential peak on the 7th day, which was shifted to the left compared to other days.

Table 1. Electrodynamic parameters of bare and PANI-modified pencil graphite electrodes (PGEs) recorded in 0.050 M $FeSO_4$ solution at a scan rate of 100 mV/s

Electrode	**Epa (mV)**	**Epc (mV)**	**ΔE (mV)**	**Ipa (µA)**	**Ipc (µA)**	**Ipa/Ipc**
Bare PGE	840	–50	890	125	–175	0.71
PANI/PGE	844.5	–200	1044.5	275	–150	1.83

Table 2. Comparison on the related reported works used pencil graphite electrode-based (PGE), polyaniline-based (PANI) for electrochemical detection of Fe^{2+}/Fe^{3+}

Modification	**Electrochemical Techniques**	**Concentration Range (M)**	**LOD (M)**	**Real Samples**	**Ref.**
Bare PGE (HB-type)	DPV	7.16×10^{-7} to 1.25×10^{-5}	1.09×10^{-6}	Water samples	[31]
PANI-based Graphite Carbon Rod	Potentiometry	5×10^{-9} to 50×10^{-6}	N/A	N/A	[32]
PANI NPs/Glassy Carbon Electrode	CV	0.06×10^{-3} to 0.2×10^{-3}	0.06×10^{-3}	N/A	[33]
PANI/PGE	CV	0.005 to 0.05	1×10^{-2}	Corroded steel	This work

This anomaly may be attributed to the undeveloped state of the sample solution at that time, preventing it from following the trend observed on subsequent days. As the immersion period progresses, the solution becomes more stable and consistent, leading to a more predictable redox behavior. Additionally, the bare PGE was not as sensitive as the PANI/PGE (**Fig. 4(B)**), where the peak on the 7th day followed the expected trend. This difference in sensitivity may be attributed to the lower conductivity of bare PGE compared to the modified PGE, which contains polyaniline, a highly conductive polymer. The peak current increased on subsequent days for both anodic and cathodic reactions, due to the enhanced electron transfer of Fe^{2+} ion [34].

The Ipa obtained from both voltammograms were substituted into the respective linear equations derived from the Fe^{2+} ion calibration curves, as described in the Calibration Curve of Fe^{2+} Standard Solution section for both PGE and PANI/PGE electrodes. This method was employed to determine the concentration of the sample solution on the respective days of analysis. **Fig. 5** illustrates the relationship between the concentration of the sample solution and the immersion time of the mild steel for bare and PANI/PGE. Both linear graphs showed a similar trend where the concentration of the sample solution increased with longer immersion times. This trend indicates that more Fe^{2+} ions accumulated in the sample solution over time. Notably, the PANI/PGE electrode demonstrated a higher detection of Fe^{2+} ions compared to the bare PGE electrode. Specifically, at 7

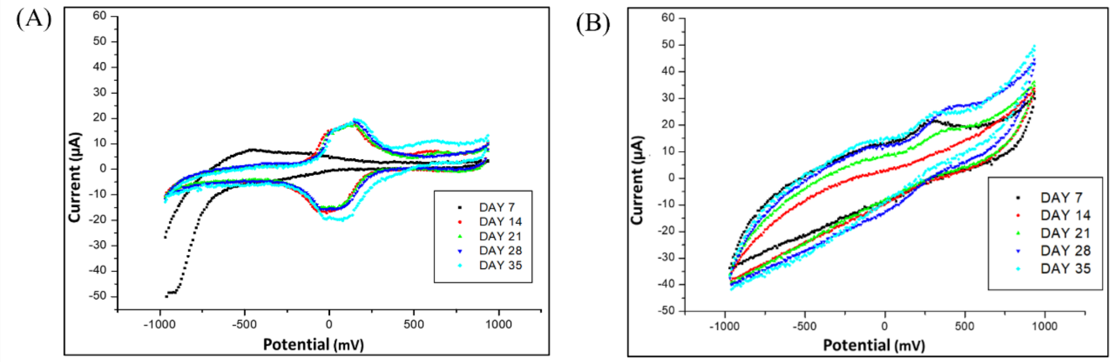

Figure 4. Cyclic voltammogram of sample solution from 7th day to 35th day for (A) bare PGE and (B) modified PGE with PANI

days, the current for the PANI/PGE electrode increased by 48%, while at 35 days, it increased by 32%, highlighting the enhanced performance of the modified electrode. However, it is important to consider that these measurements rely on the assumption of a stable, uniform passive layer on the mild steel surface. In practice, passive films may degrade over time due to delamination or localized corrosion phenomena such as pitting, leading to non-uniform Fe^{2+} ion release and potential variations in measurement accuracy. Despite these challenges, the PANI coating on the electrode provides a more reliable interface for Fe^{2+} detection. This is attributed to the redox-active nature of PANI, which enables it to participate in reversible electron transfer processes, thereby amplifying the electrochemical signal without being consumed. Additionally, the surface of PANI contains functional groups such as amine and imine, which can coordinate with Fe^{2+} ions through electron donation, improving ion capture efficiency even under conditions of uneven ion distribution caused by localized corrosion on the mild steel surface. **Table S1** summarizes the concentrations of the sample solution detected at different immersion times for both PGE and PANI/PGE.

Determination of corrosion rate

Fig. 6(A) and 6(B) exhibited the corrosion rate against immersion time for both bare PGE and PANI/PGE. Both graphs demonstrated a lower corrosion rate as the immersion time was prolonged. This reduction in corrosion rate can be attributed to the initial formation of corrosion products, which naturally slow down the progression of the corrosive medium [35]. The separation of dissolved ions from the Fe atoms beneath the film of the metal sheet immersed in NaCl solution led to the formation of a protective layer [36]. Additionally, the initial corrosion products were not removed during the observation period, allowing them to cover the mild steel surface naturally and prevent further corrosion [37]. This protective layer shielded the mild steel surface from the attack of Fe ions dissolved in the solution.

Based on **Fig. 6(A) and 6(B)**, the corrosion rate for the bare PGE increased on the 35th day, while the modified PGE with PANI showed an increase on the 28th day. This increase may be caused by the attack of aggressive Cl^- ions, which destroyed the protective layer and exposed the new surface of mild steel to the solution, leading to a sudden increase in corrosion rates [35]. The dissolved oxygen species in the NaCl solution reacted with the surface of the mild steel (Fe ions). Due to the presence of unstable ions ($Fe(OH)^+$), the Cl^- ions attacked and destroyed the protective layer of mild steel [36], as shown in the equation below:

$$Fe^{2+} + 4OH^- \rightarrow 2Fe(OH)_2 \qquad \text{(Eq. 5)}$$

$$Fe(OH)_2 + Cl^- \rightarrow Fe(OH)^+ + Cl^- + OH^- \qquad \text{(Eq.6)}$$

The presence of Cl^- ions acted as a catalyst, promoting the formation of pitting and enhancing the penetration ability of oxygen species, thereby increasing the corrosion rate. Based on **Fig. 6(B)**, the corrosion rate decreased gradually on the 35th day for the modified PGE with PANI. This could be attributed to the so-called "reversed phenomenon," where the corrosion rate reaches a dynamic balance between the attack of Cl^- ions on the mild steel surface and the protective effect of corrosion products. It was discovered that the development of corrosion products slowed the diffusion of Fe^{2+} ions dissolved in the solution to the mild steel surfaces [38]. **Table S2** summarizes the immersion days and the corresponding corrosion rates based on the type of electrode.

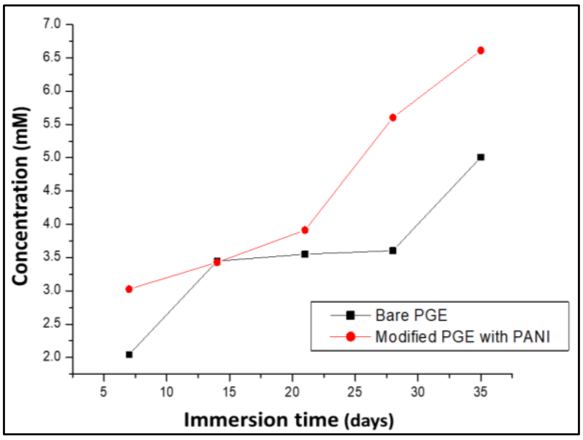

Figure 5. Relationship between the concentration of the sample solution and the immersion time of the mild steel for bare and modified PANI/PGE

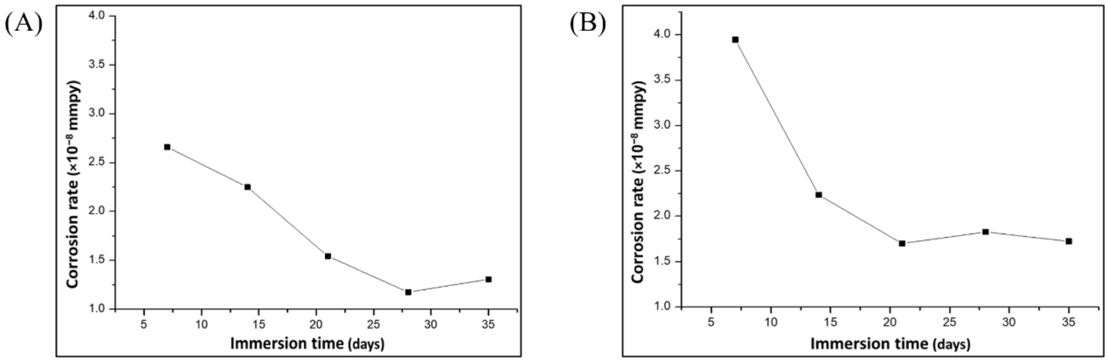

Figure 6. Corrosion rate (mmpy) against immersion time (days) for (A) bare PGE and (B) modified PGE with PANI

Conclusion

This study successfully developed a novel electrochemical sensor using a pencil graphite electrode (PGE) modified with polyaniline (PANI) for the detection of corrosion-related Fe^{2+} ions. The modified PANI/PGE electrode demonstrated a 35% increase in electroactive surface area and achieved an enhanced peak current ratio of 1.83 compared to the unmodified PGE, indicating superior conductivity and improved electron transfer kinetics. Corrosion analysis was effectively carried out via cyclic voltammetry and potentiodynamic polarization, where the Fe^{2+} concentration in mild steel samples increased progressively with immersion time. Notably, the PANI/PGE electrode exhibited 48% higher anodic current after 7 days of immersion and 32% higher after 35 days, compared to the bare PGE, confirming its enhanced analytical response. The sensor achieved a limit of detection (LOD) of 1×10^{-2} M and a limit of quantification (LOQ) of 3×10^{-2} M for Fe^{2+} ions, demonstrating its capability to detect relatively low concentrations of corrosion products in a saline environment. To the best of our knowledge, this is the first reported development of a PANI-modified pencil graphite electrode as a corrosion electrochemical sensor for the voltammetric detection of mild steel, offering a low-cost, disposable, and effective alternative for corrosion monitoring applications.

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