



## Cyclic Voltammetric Investigation of Iron In Ore at 1,10-Phenanthroline Modified Carbon Paste Electroactive Electrode

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### Abstract

An electrochemical method based on cyclic voltammetry (CV) and employing a 1,10-phenanthroline (phen) modified carbon paste electroactive electrode (OMCPEE) has been proposed for the determination of iron on solid substratum. The OMCPEE was calibrated with standard iron sulfate  $FeSO_4$  in 2 M HCl as a supporting electrolyte. Under optimized conditions, the proposed method has shown acceptable analytical performances. Two couples of well-defined redox peaks, which are corresponded to the oxidation of iron (II) and ferriox complex are recorded. The scan rate effect suggested that the electrode reaction corresponds to an adsorption-controlled process. Using the proposed method, iron was successfully determined in ore samples, suggesting that this method can be applied to the determination of iron in geological matrices.

**Keywords:** Cyclic voltammetry, Modified carbon paste electrode, 1,10-phenanthroline, Ore, Iron.

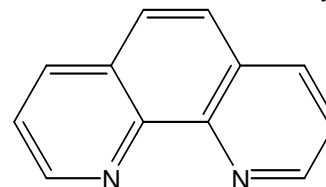
### Introduction

Iron ( $^{56}_{26}Fe$ ) is the fourth most abundant (5%) element in the earth's crust. Due to its reductive behavior, it rarely exists as native element. It is found in nature in oxidized forms ( $Fe^{2+}$  or  $Fe^{3+}$ ), combined in ores. The main ones are: magnetite, hematite<sup>1,2</sup>.

The importance of the iron industry and especially the remarkable properties of this element have attracted much attention<sup>3-5</sup>. Therefore, iron is extensively studied and many methods are reported for its exploitation that range from the characterization of ores to the extraction of the metal<sup>6,7</sup>. Despite their excellent sensitivity and selectivity, the main analytical techniques used in the analysis of iron traces in biological and environmental samples, such as flame atomic absorption spectrometry, flow injection analysis spectrophotometric (FIA) and X-ray fluorescence spectrometry are time-consuming and require expensive instruments<sup>8-11</sup>.

However, the electrochemical methods, with their easy implementation, their low cost and analytical performance, have proved to be an alternative to the detection of a number of analytes including iron<sup>12-15</sup>. Yet, for the study of inorganic solids or sparingly soluble compounds, carbon paste electroactive electrodes (CPEEs) are recommended<sup>16</sup>. In fact, the CPEEs in contrast to classical carbon paste Electrode (CPE) are obtained by direct mixing of electroactive analyte into the paste<sup>17-19</sup>. Such a device allows efficient contact between the analyte and the electrode, facilitating electron transfer at the electrochemical interface and ensuring reproducible results. Because of the electroactive compound presence, CPEEs are considered as

modified CPEs. May be for this reason, few studies on the modification of CPEEs are reported. Therefore, we believe it possible to improve the performance of those sensors by preparing modified carbon paste electroactive electrodes (MCPEEs). As for carbon paste sensors, the modification of CPEEs can be done by adding a modifying agent, which can be dissolved directly in the binder or admixed mechanically to the paste during its homogenization<sup>20-22</sup>. Chemical and biological-modifying moieties can be utilized<sup>23-26</sup>. Modified pastes offer very good properties such as high sensitivity, wide potential range, good selectivity and low detection limit<sup>27</sup>. In the literature survey, 1, 10-phenanthroline (orthophenanthroline) was used as a modifier of carbon paste electrode for the electrochemical determination of iron in aqueous solution<sup>28</sup>. Moreover, orthophenanthroline is widely used for iron pre-concentration and analysis, because of its complexing properties and its affinity with the latter<sup>29</sup>. So, this ligand can be used to modify a CPEE with iron as electroactive analyte.



Structure of 1,10-phenanthroline

In the present work, we describe the preparation of a carbon paste electroactive electrode modified with 1, 10-phenanthroline which is known to form complex with iron (II) ions, and investigate its performance for cyclic voltammetry determination of iron. We also evaluated the analytical

performance of such electrode for the characterization of the iron ions present in a sample of ore.

## Materials and Methods

**Reagent and chemicals:** All the chemicals used were of analytical grades. Iron sulfate (II)  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  was obtained from Merck.

Orthophenanthroline was purchased from LABOSI. Hydrochloric acid was purchased from Charlau. 2 M hydrochloric acid solution prepared with distilled water was used as a supporting electrolyte.

Pure graphite powder (grade II) was obtained from Johnson Matthey Chemicals limited (JMC). The natural ore sample investigated was from Kédougou in eastern Senegal.

**Apparatus:** Electrochemical measurements were performed using Potentiostat/galvanostat Uniscan Instruments PG580, interfaced with a PC under UiEchim 1.64 software.

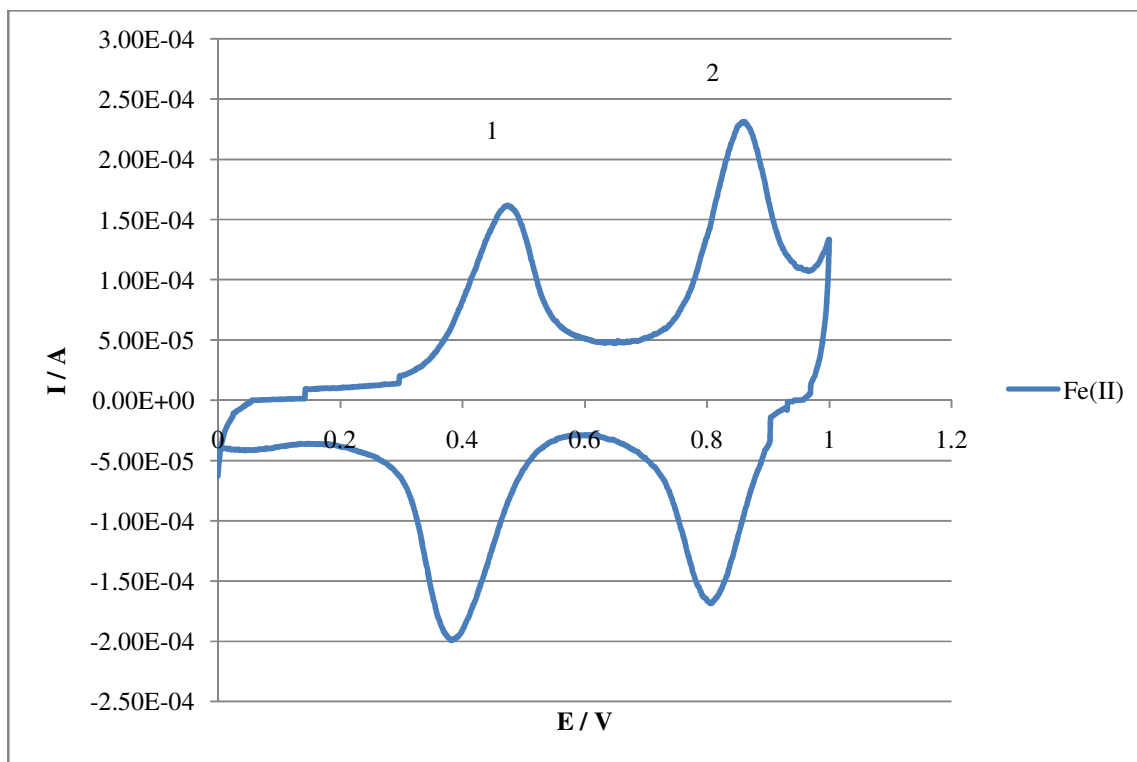
All experiments were carried out at room temperature, in a conventional three-electrode cell. The electrode system contained a working carbon paste electroactive electrode, home-made, a platinum wire as a counter electrode, and a saturated calomel electrode ( $\text{Hg}/\text{Hg}_2\text{Cl}_2/\text{KCl}, \text{sat.}$ ) as a reference electrode.

**Preparation of the working electrode:** The Orthophenanthroline Modified Carbon Paste Electroactive Electrode (OMCPEE) were prepared by hand mixing 76.8 % of graphite powder with 17.4 % of 1,10-phenanthroline powder and 5.8% of the electroactive sample ( $\text{FeSO}_4$  or Ore) finely ground with a mortar and pestle, so that the ratio analyte/orthophenanthroline is 1:3. Then, 50  $\mu\text{L}$  of 2M HCl was added to the above mixture and mixed until a uniformly wetted paste was obtained. The paste was then packed into the end of a glass tube (3.4 mm i.d.). Electrical contact was made by forcing a copper wire down into the tube.

## Results and Discussion

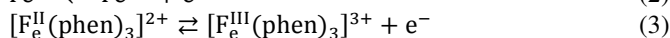
**Electrochemical behavior of the orthophenanthroline modified carbon paste electroactive electrode:** The electrochemical behavior of the carbon paste electroactive electrode modified with o-phenanthroline (phen) was studied by cyclic voltammetry using a standard sample of iron sulfate crystals ( $\text{FeSO}_4$ ). The analysis of the paste consisting of 5.8%  $\text{FeSO}_4$  was performed in the potential range from 0 to 1 V, at 0.002  $\text{Vs}^{-1}$  scan rate in 2M hydrochloric acid supporting electrolyte.

The obtained voltammogram (Figure-1) shows a cycle with two well defined pairs of peaks.



**Figure-1**  
Cyclic voltammogram of  $\text{FeSO}_4$  in 2M HCl supporting electrolyte, at OMCPEE with 0.002  $\text{Vs}^{-1}$  scan rate

A first pair that provides an anodic peak  $E_{pa1} = 0.474$  V / SCE and a cathodic peak  $E_{pc1} = 0.381$  V / SCE. This value of  $E_{pa1}$  is in perfect agreement with the oxidation peak of iron(II) oxides reported elsewhere<sup>30</sup>. Moreover, according to Hamilton and Woods, all iron formed above  $\sim 0.4$  V will be in the ferric state<sup>31</sup>. Thus, the recorded potential refers to the oxidation of iron from ferrous into ferric state, corresponding to  $Fe^{3+}/Fe^{2+}$  redox system. For the second couple, anodic and cathodic peaks appear respectively at  $E_{pa2} = 0.859$  V / SCE and  $E_{pc2} = 0.806$  V / SCE. This reflects the formation and oxidation of ferriox complex  $[Fe^{II}(phen)_3]^{2+}$ . Indeed, the redox potential is calculated as  $E^\circ = (E_{pa2} + E_{pc2})/2 = 0.833$  V / SCE. This value is in accordance with the formal potential of ferriox redox system  $[Fe^{III}(phen)_3]^{3+}/[Fe^{II}(phen)_3]^{2+}$ ,  $E^\circ = 0.82$  V / SCE<sup>32</sup>. Chen *et al.* have studied the iron(II)-iron(III) complexes with o-phenanthroline in aqueous  $H_2SO_4$  media and reported curves similar to above phenomena<sup>32</sup>. The following equations depict the reactions involved: when mixing  $Fe^{2+}$  and the ligand phen in the paste there arises the formation of a ferriox complex according to the equation 1. Moreover, a part of the iron (II) cations remains uncomplexed and undergoes an oxidation following the equation 2 and related to the first peak ( $E_{pa1}$ ). The equation 3 depicts the oxidation of the obtained complex at sufficiently high potential ( $E_{pa2}$ ).



The calculation of the potential difference between the cathodic and anodic peaks (Table-1) shows data slightly different from the Nernstian value  $0.059/n$  V for both iron and ferriox couples.

**Table-1**  
Peak potentials in the CV analysis of  $FeSO_4$  on OMCPEE, at  $0.002$  Vs<sup>-1</sup> scan rate

Ox / Red	$E_p$ (V)		
	$E_{pa}$	$E_{pc}$	$\Delta E_p$
$Fe^{3+}/Fe^{2+}$	0.474	0.381	0.093
$[Fe^{III}(phen)_3]^{3+}/[Fe^{II}(phen)_3]^{2+}$	0.859	0.806	0.053

Moreover, the ratio of peak intensities (Table-2) gives values close to 1.

**Table-2**  
Ratio of peak intensities during  $FeSO_4$  analysis

Ox / Red	$I_p$ (mA)		
	$I_{pa}$	$I_{pc}$	$ I_{pa}/I_{pc} $
$Fe^{3+}/Fe^{2+}$	0.161	-0.199	0.809
$[Fe^{III}(phen)_3]^{3+}/[Fe^{II}(phen)_3]^{2+}$	0.231	-0.169	1.367

**Electrochemical response of the ore on the OMCPEE:** After studying the behavior of the OMCPEE, we evaluated its performance by analyzing a sample of ore whose qualitative composition was determined, with a predominance of iron, in a previous paper<sup>33</sup>. Figure-2 shows the voltammogram of the electrochemical response of 5.8% of the ore (solid curve). Potential range from 0.2 to 1 V was explored at  $0.002$  Vs scan rate in the presence of 2M HCl as supporting electrolyte. Similar to those of  $FeSO_4$  results (dotted curve) were obtained. For the first pair of conjugate peaks, the anodic value  $E_{pa1} = 0.474$  V / SCE remains unchanged while the cathodic one shifts slightly ( $E_{pc1} = 0.404$  V / SCE). Concerning the second pair of peaks ( $E_{pa2} = 0.874$  V / SCE;  $E_{pc2} = 0.809$  V / SCE), both anodic and cathodic peaks shifted slightly. However, the observed phenomena correspond to reactions of the above-mentioned redox couples (reactions 2 and 3).

Potential differences ( $\Delta E_p$ ) among conjugate anodic and cathodic peaks are calculated in Table 3. The result for ferriox complex ( $\Delta E_p = 0.065$  V) is not far from the Nernstian value ( $0.059/n$  V). It can be expressed by  $\Delta E_p = \frac{0.059}{n} \pm 0.006$  V, where n represents the number of electrons involved in the reaction (3),  $n = 1$  and 0.006 is the associated uncertainty. This  $\Delta E_p$  expression applies to the same couple,  $[Fe^{III}(phen)_3]^{3+}/[Fe^{II}(phen)_3]^{2+}$  obtained with the  $FeSO_4$  sample.

**Table-3**  
Difference of peak potentials in the CV analysis of ore at  $0.002$  Vs<sup>-1</sup> scan rate

Ox / Red	$E_p$ (V)		
	$E_{pa}$	$E_{pc}$	$\Delta E_p$
$Fe^{3+}/Fe^{2+}$	0.474	0.404	0.070
$[Fe^{III}(o-phen)_3]^{3+}/[Fe^{II}(o-phen)_3]^{2+}$	0.874	0.809	0.065

However, this remark does not apply to the  $Fe^{3+}/Fe^{2+}$  couple for which both  $FeSO_4$  and ore samples give values which are more distant from  $0.059/n$  V, where  $n=1$  (equation 2 and 3).

By calculating the current intensities ratios of anodic and cathodic peaks, the results reported in Table-4, show values close and higher to 1, respectively for iron and ferriox redox system.

**Table-4**  
Ratio of peak intensities in the CV analysis of ore on OMCPEE, at  $0.002$  Vs<sup>-1</sup> scan rate

Ox / Red	$I_p$ (mA)		
	$I_{pa}$	$I_{pc}$	$ I_{pa}/I_{pc} $
$Fe^{3+}/Fe^{2+}$	0.202	-0.340	0.594
$[Fe^{III}(phen)_3]^{3+}/[Fe^{II}(phen)_3]^{2+}$	0.459	-0.267	1.719

All above considerations reflect quasi-reversible systems for both redox couples  $\text{Fe}^{3+}/\text{Fe}^{2+}$  and  $[\text{Fe}^{\text{III}}(\text{phen})_3]^{3+}/[\text{Fe}^{\text{II}}(\text{phen})_3]^{2+}$ .

**Effect of potential scan rate:** To further understand the electrode process, the scan rate effect was studied. Figure 3 shows the cyclic voltammograms of ore on OMCPEE, in 2 M HCl with scan rate ranging from 1 to  $5\text{mVs}^{-1}$ . Both anodic and

cathodic peak currents of ferroin (peak 2) enhanced with the increase of scan rate. Only the oxidation peak potential shifted to more positive potentials. However, for the iron couple (peak 1), only anodic peak currents decrease with increasing sweep rate, and at the same time the oxidation peak potentials shifted positively.

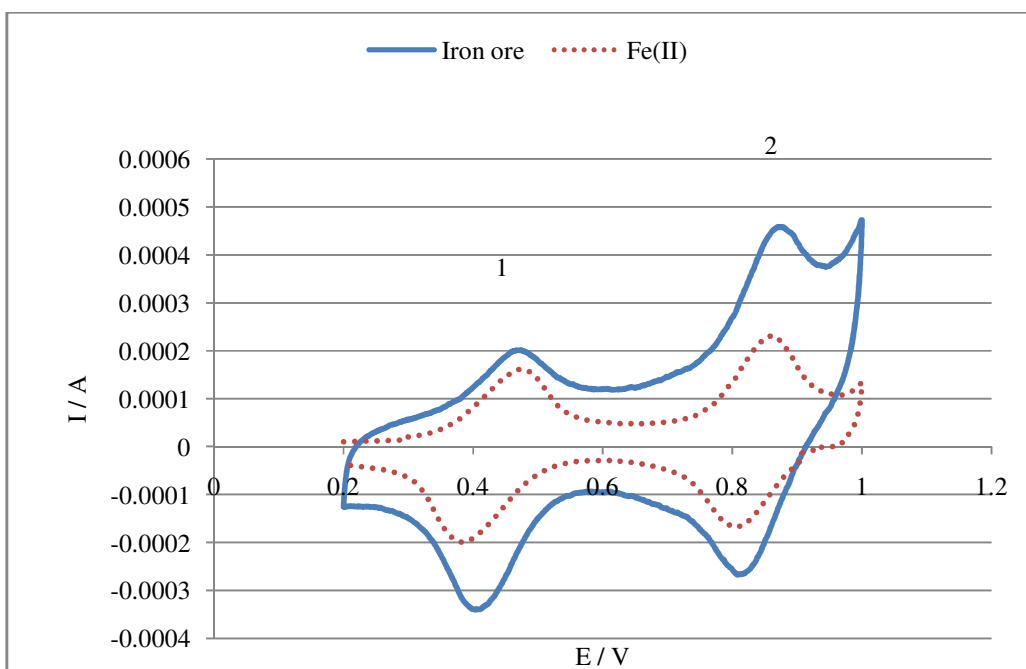


Figure-2

CVs of  $\text{FeSO}_4$  (...) and ore (—), in 2M HCl supporting electrolyte, at OMCPEE with  $0.002\text{Vs}^{-1}$  scan rate

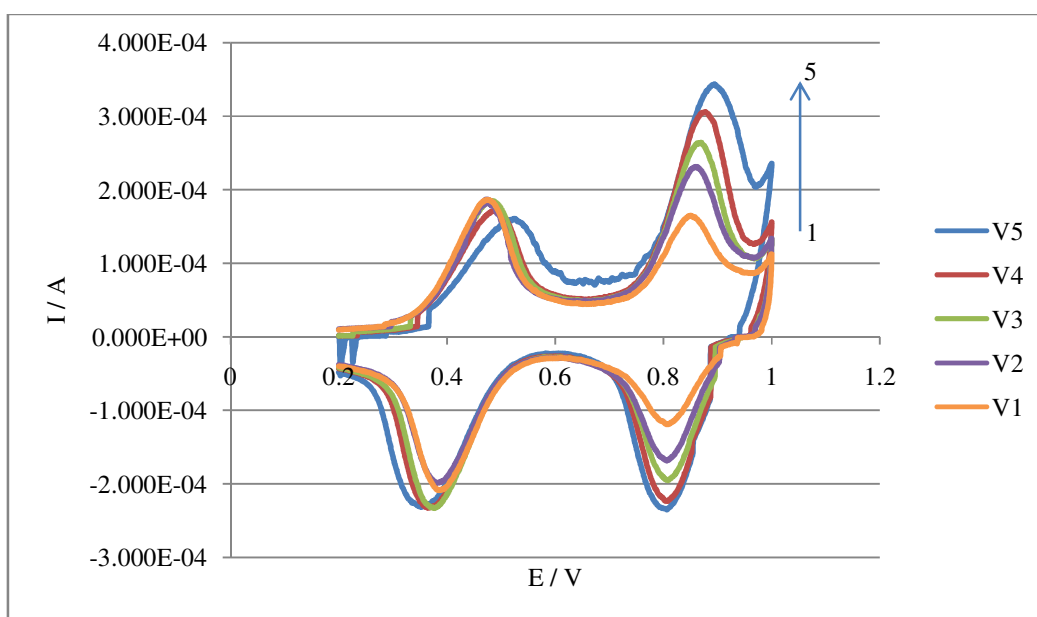


Figure-3

CVs of iron ore at different scan rates,  $1 - 5\text{mVs}^{-1}$

Also, a plot of peak current ( $I_p$ ) versus scan rate ( $v$ ) was found to be linear for both anodic and cathodic currents in the case of ferriin couple (Figure-4) and only for oxidation current in the case of iron couple (Figure-5), indicating that the process is adsorption-controlled.

### Conclusion

In the present paper, we have prepared a chemically modified electrode by incorporating orthophenanthroline in the matrix of carbon paste electrode. The electrochemical behavior of iron (II) ions at the surface of the prepared modified electrode was

successfully investigated by CV. The analysis shows that two redox couples have reacted in two distinct potential ranges. A first zone from 0.2 to 0.6 V reveals two corresponding peaks related to electronic exchanges between the  $Fe^{3+}/Fe^{2+}$  redox couple. A second area from 0.6 to 1 V, indicates the ferriin complex formation, involving the couple  $[Fe^{III}(phen)_3]^{3+}/[Fe^{II}(phen)_3]^{2+}$ . The redox systems involved are quasi reversible. The proposed method showed good analytical performances, a low cost and therefore, it can be proposed for the exploration of iron in ore.

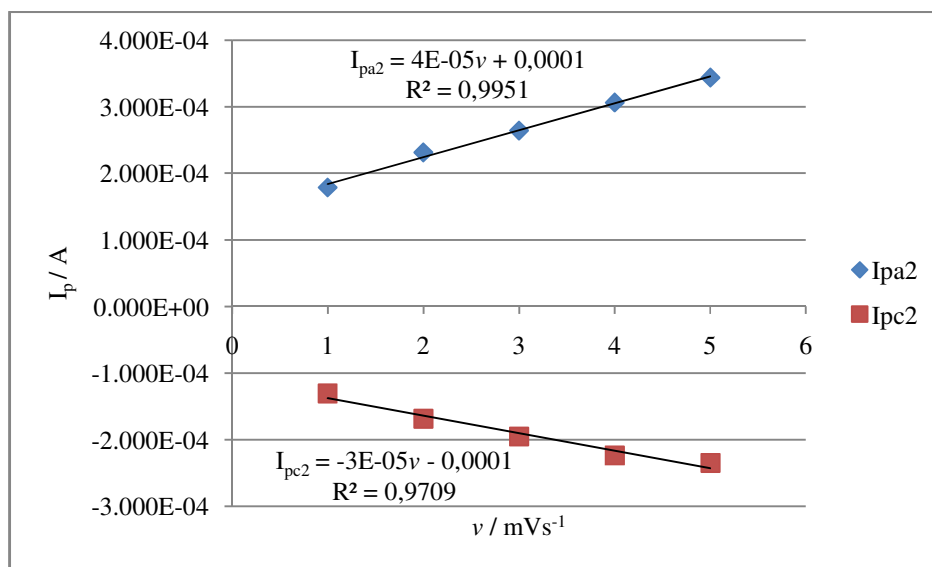


Figure-4  
 Plot of ferriin peak current versus scan rate

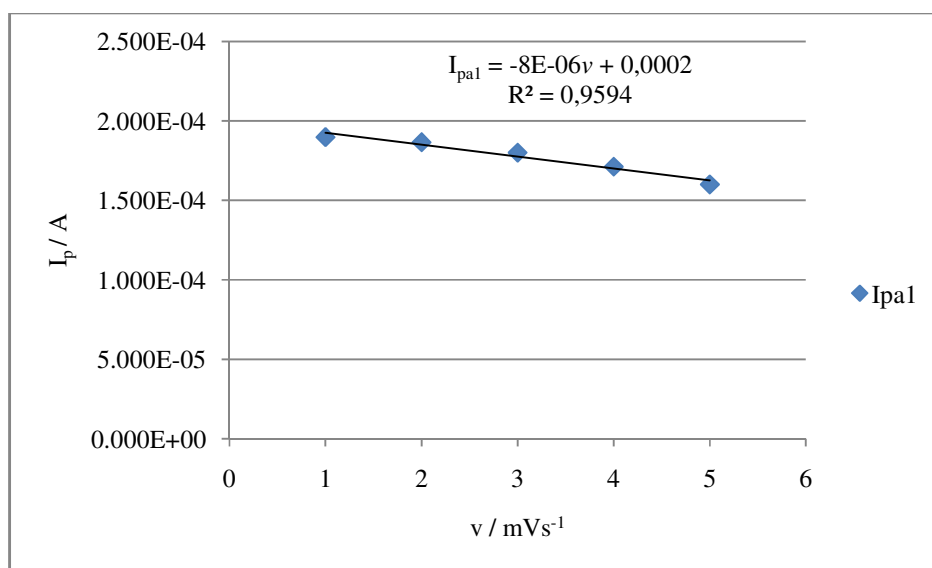


Figure-5  
 Plot of iron peak current versus scan rate

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