

## Voltammetric analysis of ascorbic acid using a natural phosphate modified carbon paste electrode

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### ABSTRACT

This paper describes the development, electrochemical characterization and utilization of novel modified natural phosphate carbon paste modified electrode (NP-CPE) for the electrocatalytic determination of ascorbic acid (AA). The electrochemical profile of the proposed modified electrode was analyzed by cyclic voltammetry (CV) and Square Wave Voltammetry (SWV). The influence of variables such the concentration of ascorbic acid adsorbed onto NP, and the pH of solution were tested. The capacity of prepared electrode (NP-CPE) for selective detection of AA was confirmed in a sufficient amount of ascorbic acid.

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### KEYWORDS

Ascorbic acid;  
Carbon paste electrode;  
Cyclic voltammetry;  
Square wave voltammetry;  
Electrochemical detection.

### INTRODUCTION

Ascorbic acid (AA) scheme 1, also known as vitamin C, is one of the most important vitamins widely exist in various plants and takes part in some important biological reactions such as free radical scavenging, cancer preventing and improving immunity. This compound exists widely in food, plant and animal tissues, but cannot be synthesized by the human body. A recommended daily intake of AA is about 70–90 mg. Inadequate intake will result in the symptoms of scurvy, gingival bleeding, and so on; excess AA intake will also lead to urinary stone, diarrhea and stomach convulsion<sup>[1]</sup>. Due to the importance of AA in life cycle, its determination in aqueous solution is very important. Traditional procedures for AA determination are generally based on enzymatic methods<sup>[2]</sup>, on titration with oxidizing

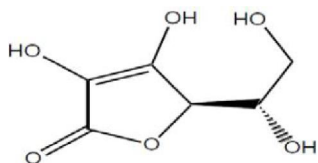
agents, like iodine or 2, 6-dichlorophenolindopheno and HPLC analysis with fluorimetric<sup>[3]</sup> or UV–vis detection<sup>[4]</sup>. Recently there is a considerable interest to develop chemical sensors for electrochemical detection of AA. AA can be easily oxidized electrochemically at conventional electrodes which have been used to detect AA<sup>[5,6]</sup>. However, direct oxidation of ascorbic acid at bare electrode requires high over-potential which results in electrode fouling by its oxidation products with poor reproducibility, low selectivity and sensitivity. In addition, some of biological molecules, e.g. dopamine and uric acid, undergo oxidation within same potential window as AA. To dissolve these problems, chemically modified electrodes have been developed and reported with various functional materials such as conducting polymers<sup>[7–11,23]</sup>, ionic liquid<sup>[12,13]</sup>, metal nanoparticles<sup>[8]</sup>, carbon nanotubes<sup>[9,13,14]</sup> and macro-

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cyclic compounds<sup>[15,16]</sup>. Xanthurenic acid (Xa) is a product of the tryptophan–NAD pathway. It is related to various pathological conditions; although the biological function of this compound remains obscure<sup>[17–20]</sup>. Xa acts as a potent iron chelator and has been shown to have prooxidant actions<sup>[20,26]</sup>. This compound can form a variety of possible dimers after oxidation, leading to radicals or cations, which can couple with phenoxy radicals, with other dimer radicals or with unconverted compounds to produce polymers adhering strongly to the electrode surface, as evidenced for other phenols<sup>[21–25]</sup>. Therefore, an investigation into the use of the Xa-modified electrode to oxidize important antioxidants, especially for AA, is a worthwhile endeavor.

Electrochemical sensing has been proven as an inexpensive and simple analytical method with remarkable detection sensitivity, reproducibility, and ease of miniaturization.

In this work, we describe the electrochemical analysis of ascorbic acid on a natural phosphate modified carbon paste electrode (NP-CPE). The electrochemical characterization of adsorbed electroactive AA was evaluated using cyclic voltammetric (CV), square wave voltammetry (SWV) and Electronic Impedance Spectroscopy (EIS) analysis.



Scheme 1: Structural formula for L-Ascorbic acid

## EXPERIMENTAL

### Apparatus and software

Voltammetric experiments were performed using a voltalab potentiostat (model PGSTAT 100, Eco Chemie B.V., Utrecht, The Netherlands) driven by the general purpose electrochemical systems data processing software (voltalab master 4 software) run under windows 2007. The three electrode system consisted of a chemically modified carbon paste electrode as the working electrode a saturated calomel electrode (SCE) serving as reference electrode and platinum as an auxiliary elec-

trode.

### Electrodes

Modified electrodes were prepared by mixing a carbon powder and the desired weight of natural phosphate. The body of the working electrode for voltammetric experiments was a PTFE cylinder that was tightly packed with carbon paste. The geometric area of this electrode was 0.1256 cm<sup>2</sup>. Electrical contact was made at the back by means of a bare carbon.

### Procedure

The initial working procedure consisted of measuring the electrochemical response at NP-CPE at a fixed concentration of AA. Standard solution of AA was added into the electrochemical cell containing 100 mL of supporting electrolyte.

The mixture solution was kept for 20 s at open circuit and deoxygenated by bubbling pure nitrogen gas prior to each electrochemical measurement.

The cyclic voltammetry was recorded in the range from -0.6 V to 1.5 V.

The square wave voltammetry (SWV) was recorded in the range from -0.6 V to 1.5 V, for which the scan rate is 1 mV.s<sup>-1</sup>, step potential 50 mV, amplitude 2 mV and duration 0.1 s.

Optimum conditions were established by measuring the peak currents in dependence on all parameters. All experiments were carried out under ambient temperature.

## RESULTS AND DISCUSSION

### Surface characteristics

The surface structure of natural phosphate electrode was observed using scanning electron microscopy Figure 1.

### Voltammetric and EIS of paracetamol

#### (a) Cyclic voltammetry

Figure 2 shows a cyclic voltammograms (CV) in the potential range -0.6 V to 1.5 V recorded, respectively, for carbon paste and natural phosphate modified carbon paste electrode at 100 mV.s<sup>-1</sup>. The voltammograms take different forms. No peak is ob-

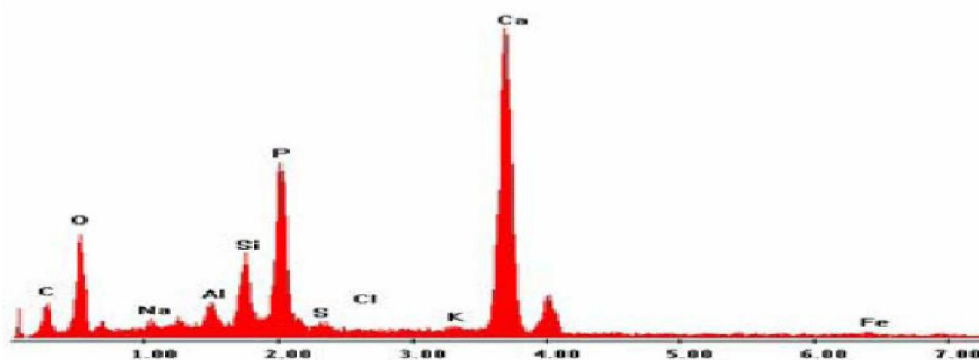
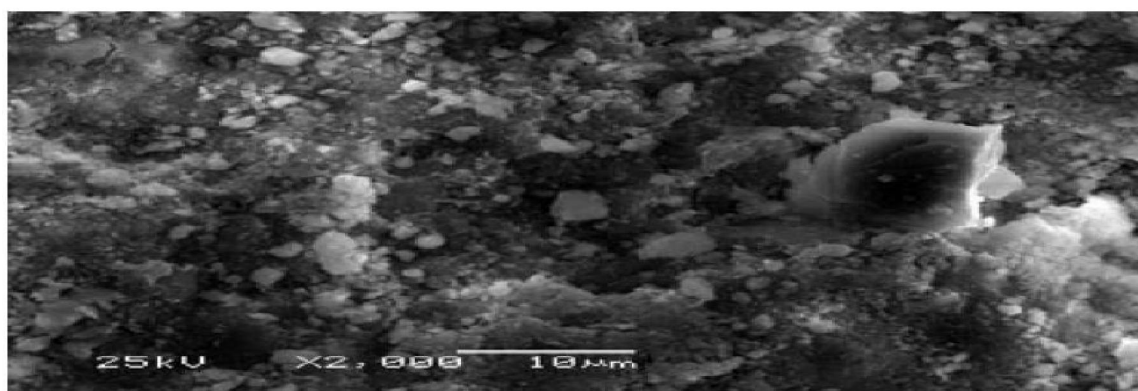


Figure 1 : Scanning electron micrograph of natural phosphate

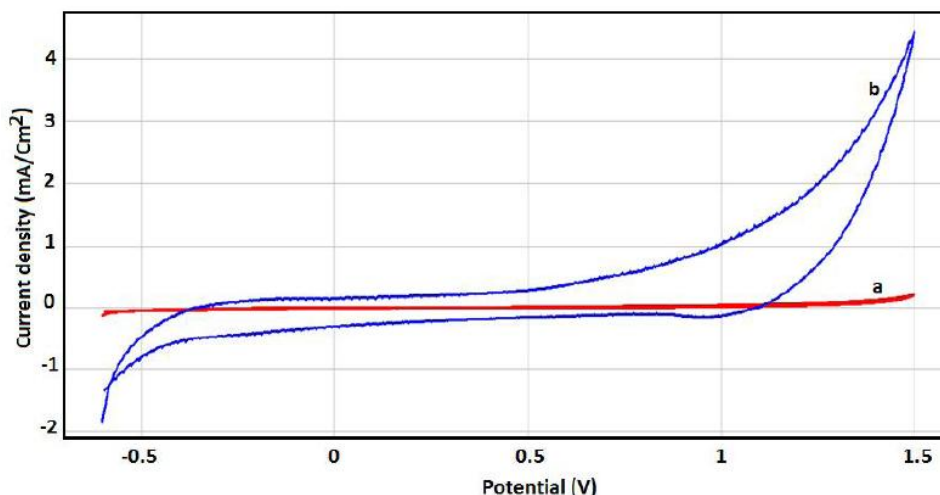


Figure 2 : Cyclic voltammograms recorded for CPE (a) and bare NP-CPE (b), in 0.1 M  $\text{Na}_2\text{SO}_4$  at 100 mV/s

served in the case of NP-CPE, it is recognized that carbon surface was effectively modified by NP.

The voltammograms of the  $\text{Na}_2\text{SO}_4$  buffer as well as 2.27mM ascorbic acid in the buffer are shown as I and II in Figure 3. No anodic peak current was observed in the voltammogram of the buffer but was observed at 0.38V in the 2.27 mM ascorbic acid solution in the buffer as shown in II of Figure 3. No cathodic peak current was found indicating an irrevers-

ible heterogenous charge transfer in this system.

The scheme 2 shows the oxidation of L-ascorbate to dehydro-L-ascorbic acid involves the transfer of two electrons and one proton<sup>[27,28]</sup>.

#### (b) Square wave voltammetry

Figure 4 shows the square wave voltammetry recorded for 2.64mM AA at bare NP-CPE in  $\text{Na}_2\text{SO}_4$  buffer solution at pH 7, This figure shows an oxidation peak potential at 0.3V.

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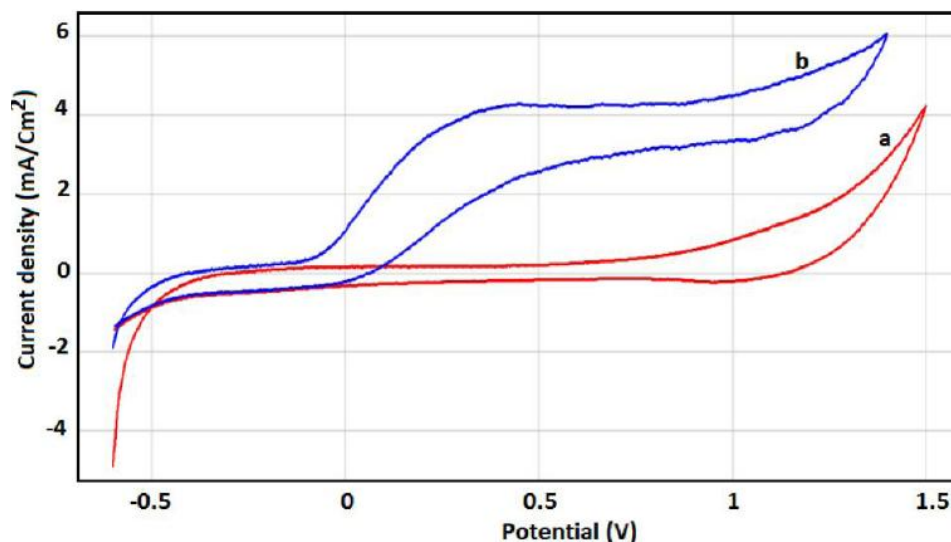
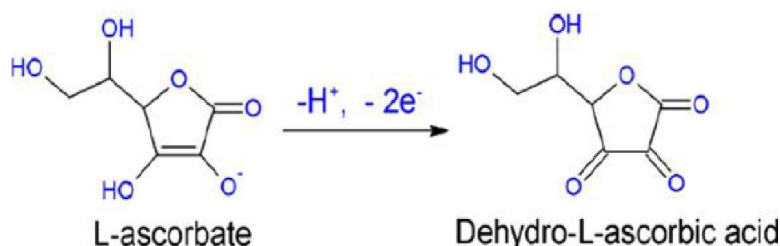


Figure 3 : CVs recorded for 2.27 mM AA at pH=7 at bare NP-CPE (a) and NP-CPE/AA (b), scan rate 100 mV/s, preconcentration time (tp)= 2min



Scheme 2 : Mechanism of electrochemical oxydation reaction of AA at NP/CPE

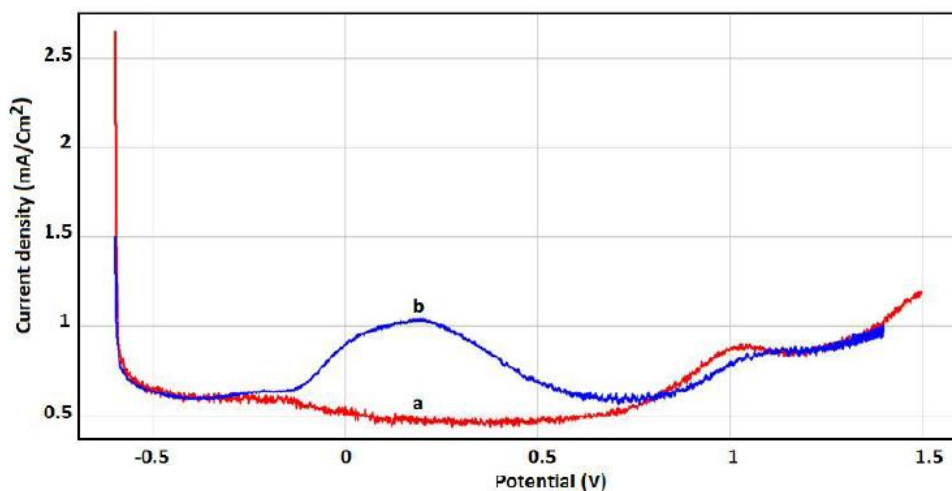


Figure 4 : SWV recorded for 2.27 mM AA at pH=7 at bare NP-CPE (a) and NP-CPE/AA (b), preconcentration time (tp)= 2min

### (c) Electrochemical impedance spectroscopy (EIS)

An impedance spectroscopy study was performed in order to confirm the results obtained by the cyclic voltammetry tests. Figures 5 and 6 show the impedance diagrams recorded for NP-CPE and NP-CPE/AA (5.68mM) respectively. at the absence of AA EIS

is right which means that there is a diffusion at the surface of the NP-CPE, for the presence of AA the impedance curve is in the form of half-circle which can be attributed to the electron transfer step.

### Optimization of experimental conditions

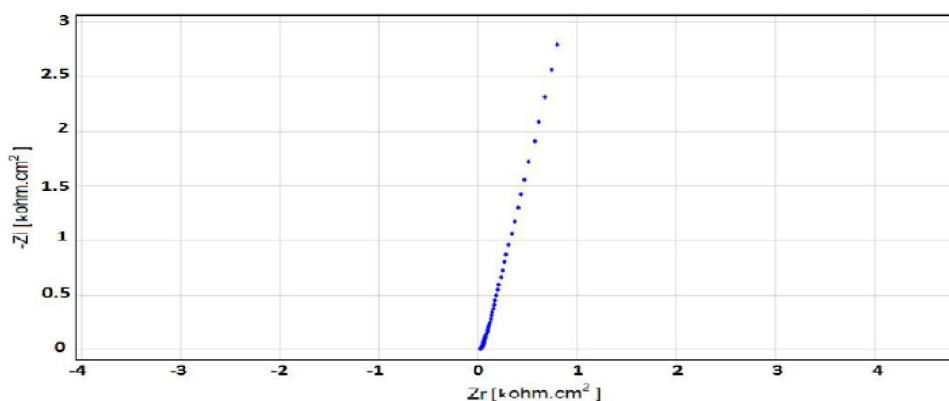


Figure 5 : Electrochemical impedance spectroscopy for NP-CPE in 0.1M  $\text{Na}_2\text{SO}_4$  solution, at open circuit potential

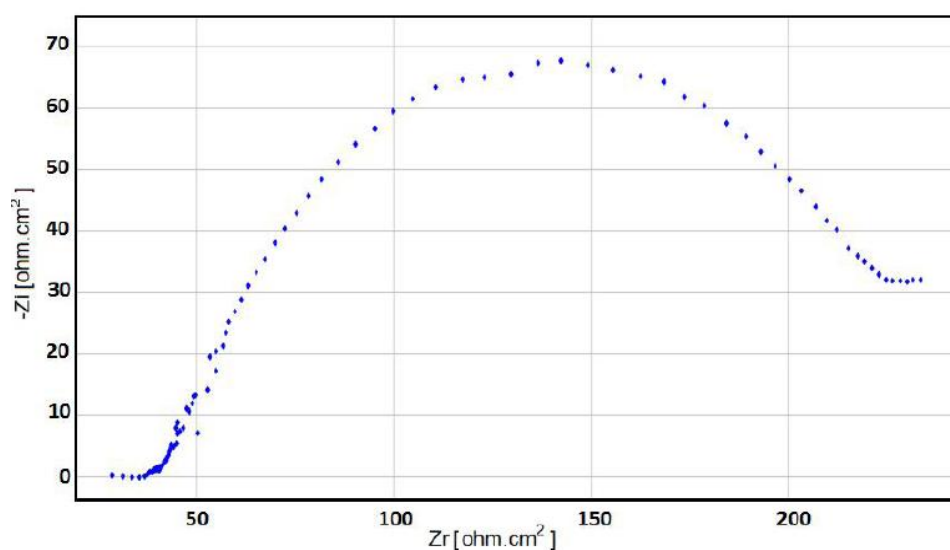


Figure 6 : Electrochemical impedance spectroscopy for NP-CPE/AA (5.26mM) in 0.1M  $\text{Na}_2\text{SO}_4$  solution, at open circuit potential

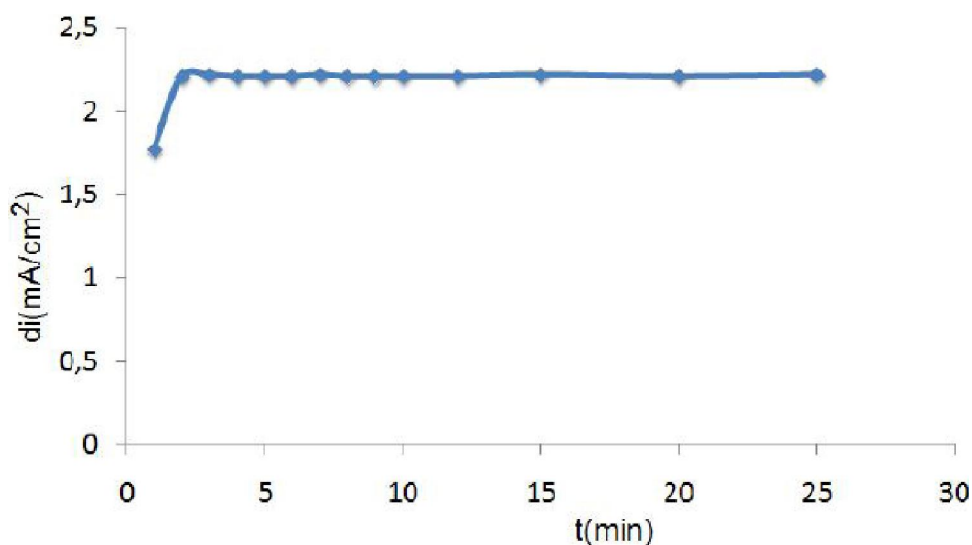


Figure 7 : Effects of accumulation time on oxidation peak currents of  $2.27 \text{ mmol L}^{-1}$  AA (pH=7) at NP-CPE, supporting electrolyte is  $\text{Na}_2\text{SO}_4$  0.1M



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Optimum conditions for the electrochemical response were established by measuring the peak current in dependence on all parameters.

### (a) Influence of accumulation time

Figure 7 shows the effect of the accumulation time, this significantly affects the oxidation peak current of AA. The peak current of  $2.27 \text{ mmol L}^{-1}$  AA increases greatly within the first 2 min. Further increase in accumulation time does not increase the amount of AA at the electrode surface owing to surface saturation, and the peak current remains constant. This phenomenon is due to the cavity structure of NP-CPE that improves the ability of the electrode to adsorb electroactive AA. Maybe this is attributed to the saturated adsorption of AA on the

NP-CPE surface. Taking account of sensitivity and efficiency, accumulation time was 6 min in the following experiments.

### (b) Effect of scan rate

The influences of scan rate on the oxidation peak potential ( $E_p$ ) and, peak current ( $I_p$ ) of AA, ( $0.1 \text{ M Na}_2\text{SO}_4$ ,  $\text{pH}=7$ ) were studied by cyclic voltammetry. The Figure 8 shows both the anodic currents linearly increase with the scan rate over the range of 60 to  $160 \text{ mVs}^{-1}$ , the oxidation potential of AA moves to positive values, suggesting that the electron transfers for AA at the natural phosphate modified CPE is adsorption controlled reaction. The Figure 9 shows the linear relationship between the scan rate anodic peak currents of AA at NP/CPE.

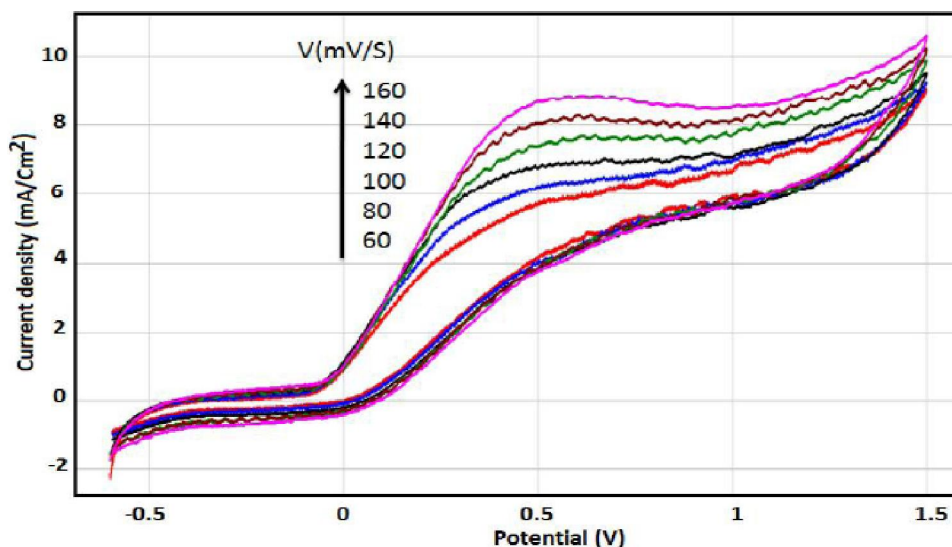


Figure 8 : CVs acquired on NP-CPE with  $4.5 \text{ mM}$  AA in the buffer solution at different scan rates from  $60$  to  $160 \text{ mV}\cdot\text{s}^{-1}$ . Inset is the plot of the peak current of AA versus scan rate

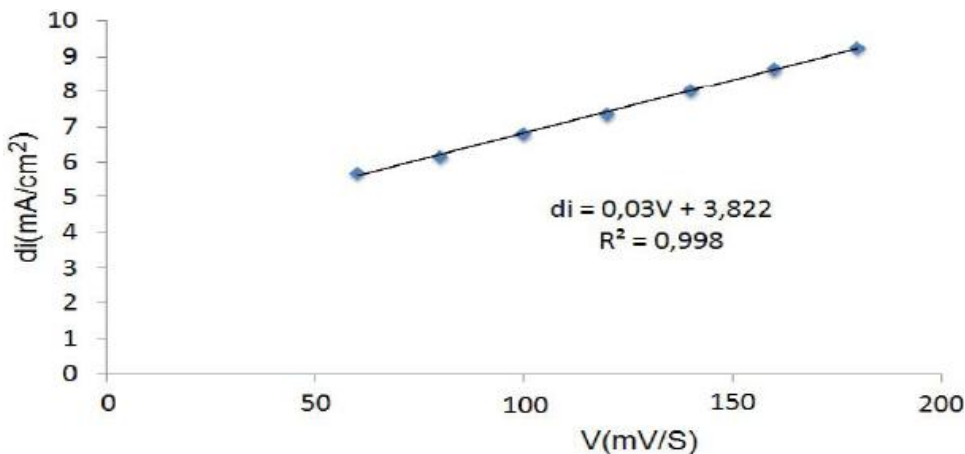


Figure 9 : Plot of peaks area versus scan rate

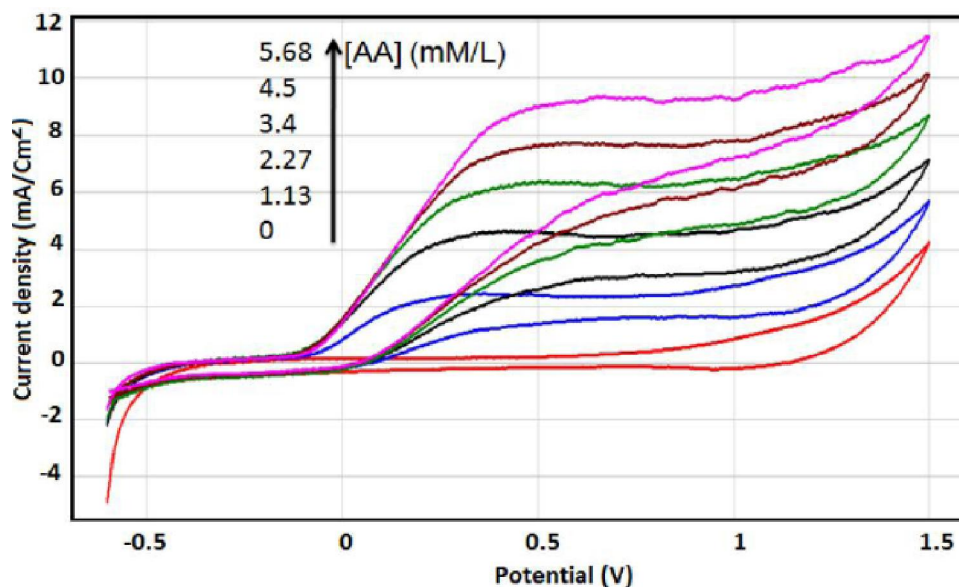


Figure 10 : Cyclic voltammograms of different concentration of AA (1.13mM to 5.68mM) at NP/CPE in 0.1 M  $\text{Na}_2\text{SO}_4$  pH=7, Scan rate 100 mV/s

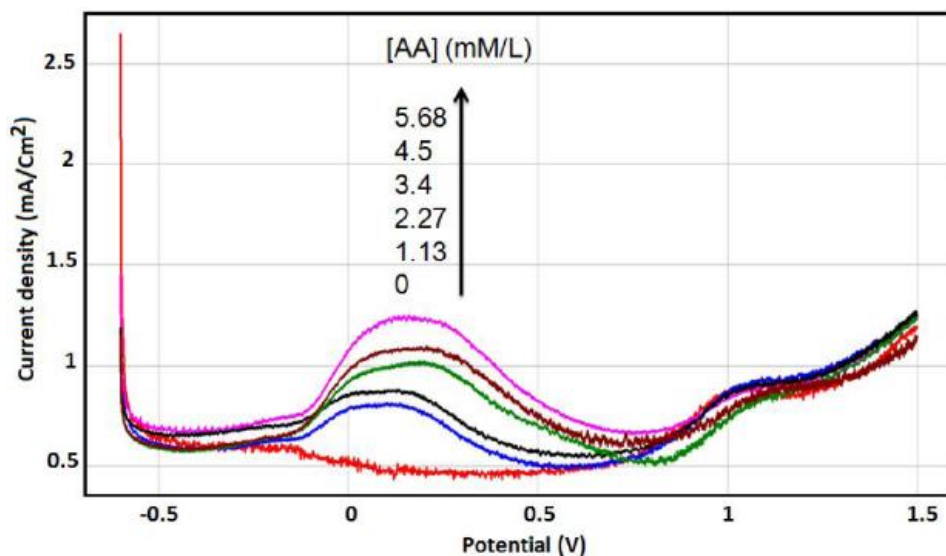


Figure 11 : Square wave voltammograms of different concentration of AA (1.13mM to 5.68mM) at NP/CPE in 0.1 M  $\text{Na}_2\text{SO}_4$  pH=7

### (c) Calibration graph

In order to obtain an analytical curve for the developed sensor, we carried out cyclic voltammograms for oxidation of AA at different concentrations in 0.1 mol  $\text{L}^{-1}$   $\text{Na}_2\text{SO}_4$  (pH=7) at a sweep rate of 100  $\text{mVs}^{-1}$ . Figure 10 and 11 shows the CV and SWV curves of different concentration respectively of AA at NP/CPE were increased from 1.13 mM to 5.68 mM. The anodic peak current increases linearly with the concentration of AA (Figure 12). These results show that ascorbic acid concentration can be measured quantita-

tively by cyclic voltammetry.

Figure 13 shows the behavior of impedance diagrams recorded for natural phosphate modified carbon paste electrode in buffer solution, in the presence of different concentrations of AA compound. We conclude that modified electrode reacts with the studied compound.

### (d) Effect of pH

The effect of varying pH on the current response of NP modified carbon paste electrode at constant ascor-

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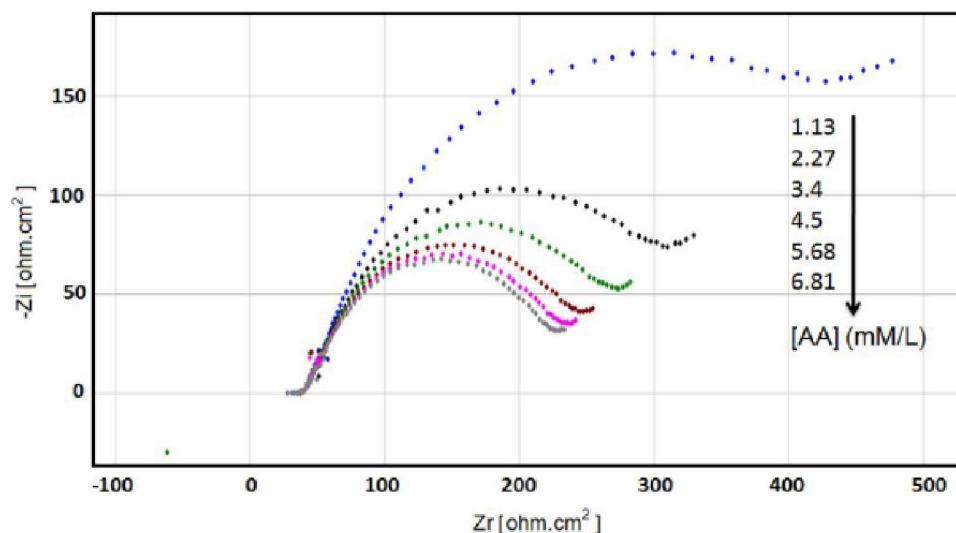


Figure 13 : Nyquist diagrams of NP modified carbon electrode, in presence of different concentrations of AA, at open circuit potential

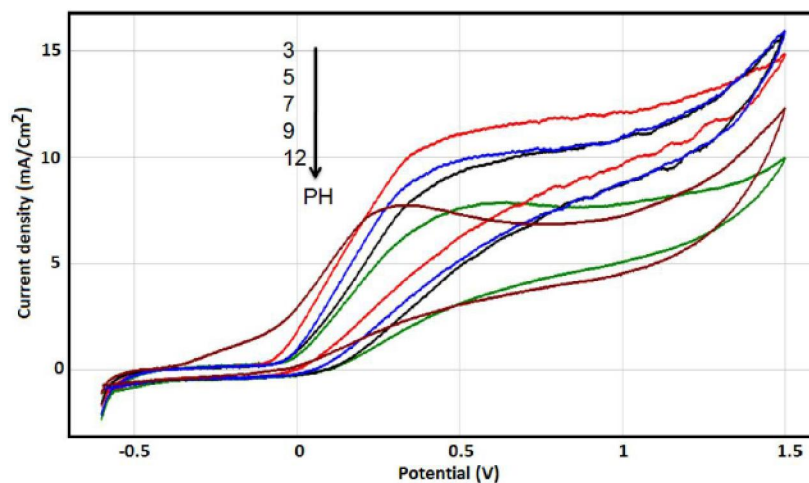


Figure 14 : CV of effect of pH on the oxidation of AA at the NP modified CPE

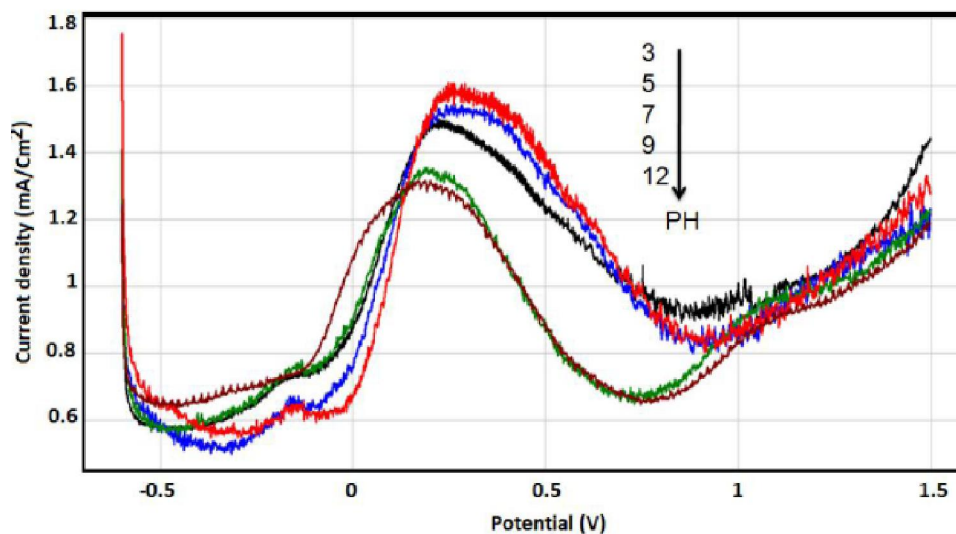


Figure 15 : SWV of effect of pH on the oxidation of AA at the NP modified CPE



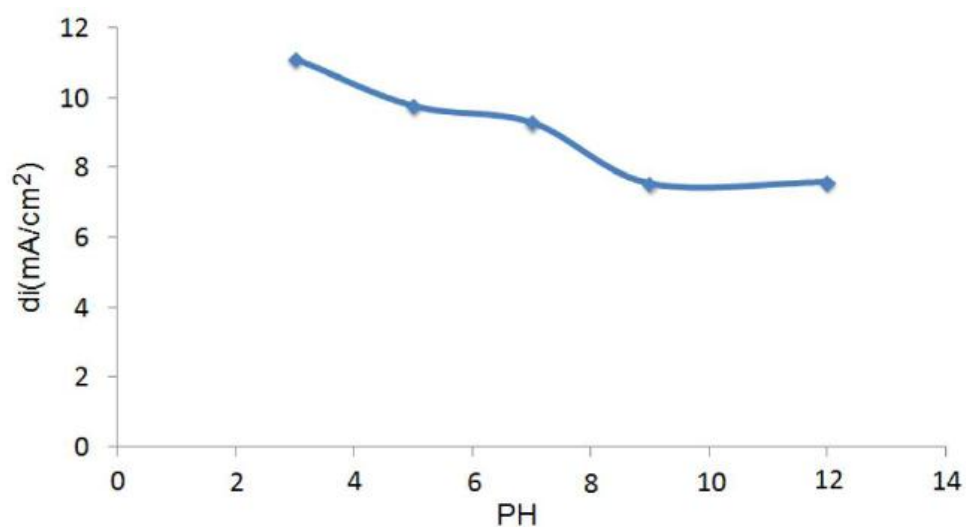


Figure 16 : Plot of the relationship between solution pH and the oxidation peak current

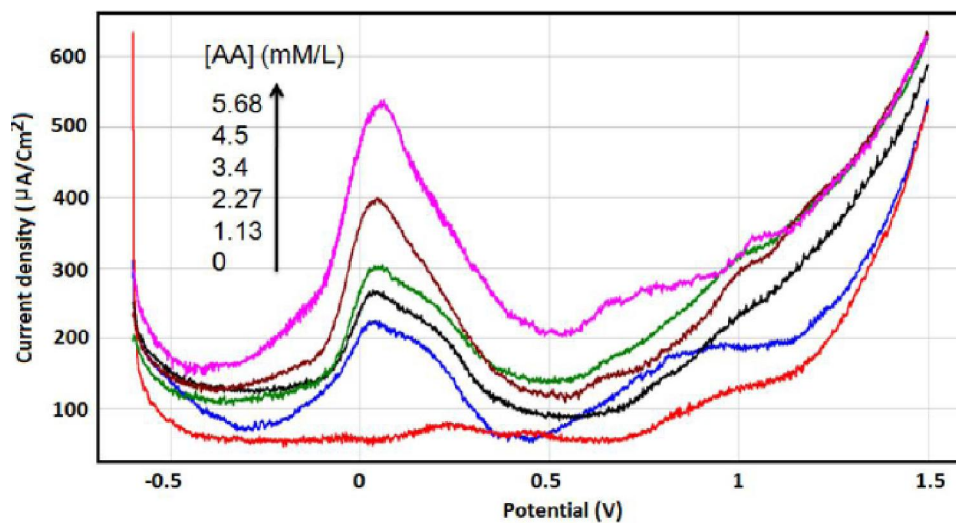


Figure 17 : Square wave voltammograms of different concentration of AA (1.13mM to 5.68mM) at NP/CPE in 0.1M Na<sub>2</sub>SO<sub>4</sub>

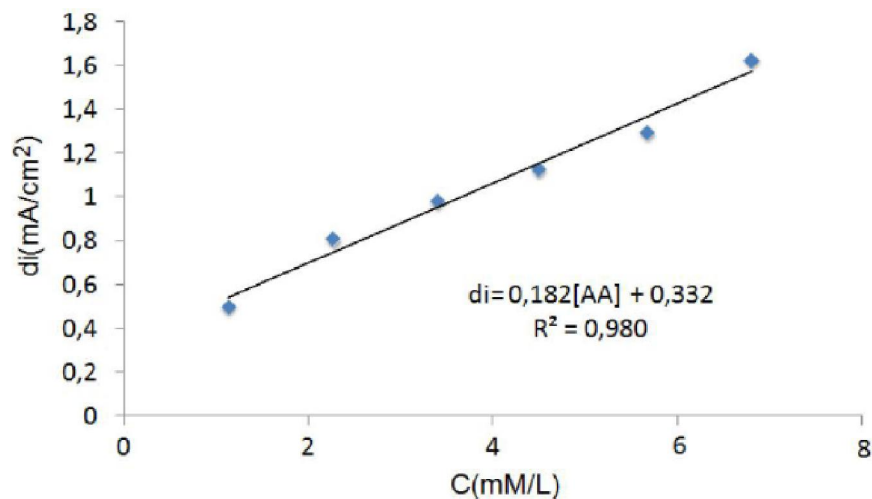


Figure 18 : Plot of peaks area versus added concentration of AA

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bic acid concentration (6.81 mM) is shown in Figures (14,15,16).

### ANALYTICAL APPLICATION

In order to evaluate the performance of NP-CPE by practical analytical applications, the determination of AA was carried out in A vitamin C tablet is finely powdered. The analytical curves were obtained by SWV experiments in supporting electrode Figure 17. It was founded that the peaks currents increase linearly versus AA added into the buffer solution Figure 18.

### CONCLUSION

We have demonstrated the use of phosphate modified carbon paste electrode for a greatly CV and SWV sensing of AA compounds. The modified electrode increased the amplitude of the current signal of AA and produced good response. The oxidation of this compound on the modified electrode occurs in an irreversible manner. The electrode construction was extremely simple and with low cost. No unstable or toxic reagents were used.

### REFERENCES

- [1] G.Hua, Y.Guo, Q.Xue, S.Shao; *Electrochim.Acta*, **55**, 2799–2804 (2010).
- [2] N.B.Saari, A.Osman, J.Selamat, S.Fujita; *Food.Chem.*, **66**, 57–61 (1999).
- [3] Z.H.Liu, Q.L.Wang, L.Y.Mao, R.X.Cai; *Anal.Chim.Acta*, **413**, 167–173 (2000).
- [4] T.P.Ruiz, C.M.Lozano, V.Tomas, J.Fenol; *Analyst*, **126**, 1436–1439 (2001).
- [5] J.B.Raoof, R.Ojani, A.Kiani; *J.Electroanal.Chem.*, **515**, 45–51 (2001).
- [6] J.M.Zen, D.M.Tsai, A.S.Kumar, V.Dharuman; *Electrochem.Comm.*, **2**, 782–785 (2000).
- [7] P.Kalimuthu, S.A.Jone; *J.Chem.Sci.*, **123**, 349–355 (2011).
- [8] D.Manoj, D.Satheesh, J.Santhanalakshmi; *Trans. Indian Inst.Met.*, **64**, 195–198 (2011).
- [9] D.Ragupathy, J.J.Park, S.C.Lee, J.C.Kim, P.Gomathi; *Macromol.Res.*, **19**, 764–769 (2011).
- [10] P.R.Roy, T.Okajima, T.Ohsaka; *J.Electroanal.Chem.*, **561**, 75–82 (2004).
- [11] L.Lin, J.H.Chen, H.Yao, Y.Z.Chen, Y.J.Zheng, X.H.Lin; *Bioelectrochemistry*, **73**, 11–17 (2008).
- [12] Y.Zhao, Y.Gao, D.Zhan, H.Hui, Q.Zhao, Y.Kou, Y.Shao, M.Li, Q.Zhuang, Z.Zhu; *Talanta*, **66**, 51–57 (2005).
- [13] Y.Chen, X.P.Chen, Z.Y.Lin, H.Dai, B.Qiu, J.J.Sun, L.Zhang, G.N.Chen; *Electrochem.Comm.*, **11**, 1142–1145 (2009).
- [14] C.G.Hu, W.L.Wang, B.Feng, H.Wang; *Int.J.Mod. Phys.B*, **19**, 607–610 (2005).
- [15] V.S.Ijeri, P.V.Jaiswal, A.K.Srivastava; *Anal.Chim. Acta*, **439**, 291–297 (2001).
- [16] B.O.Agboola, S.L.Vilakazi, K.I.Ozoemena; *J.Solid State Electrochem.*, **13**, 1367–1379 (2009).
- [17] K.S.Rogers, C.Mohan; *Biochem.Med.Metab.Biol.*, **52**, 10–17 (1994).
- [18] H.Z.Malina, X.D.Martin; *Graefes Arch.Clin. Exp.Ophthalmol.*, **234**, 723–730 (1996).
- [19] G.Thiagarajan, E.Shirao, K.Ando, A.Inoue, D.Balasubramanian; *Photochem.Photobiol.*, **76**, 368–372 (2002).
- [20] K.Murakami, M.Haneda, M.Yoshino; *Biometals*, **19**, 429–435 (2006).
- [21] J.Haccoun, B.Piro, V.Noël, M.C.Pham; *Bioelectrochemistry*, **68**, 218–226 (2006).
- [22] A.Hirano, M.Suzuki, M.Ippommatsu; *J. Electrochem.Soc.*, **139**, 2744–2751 (1992).
- [23] A.Sadiki Lamari, A.El fattouh, S.El qouatli, R.Najih, A.Chtaini; *Acta Technica*.
- [24] S.El Qouatli, R.T.Ngono, R.Najih, A.Chtaini; *Zaštita Materijala*, **52**, 4 (2011).
- [25] Harouna Massai, Benguella Benoit, Mbadcam Joseph Ketcha, Abdelilah Chtaini; *Bulletin of the catalysis society of india*, **2**, 64–68 (2009).
- [26] J.C.Miller, J.N.Miller; *Analyst, Corviniensis – Bulletin of Engineering Tome VI (Year 2013) ISSN 2067-3809*, **113**, 1351 (1988).
- [27] A.Malinauskas, R.Garjonyte, R.Mazeikiene, I.Jureviciute; *Talanta*, **64**, 121 (2004).
- [28] A.Sadiki Lamari, A.Ei Fattouh, S.Ei Qouatli, R.Najih, A.Chtaini; *Ac Technica Corviniensis – Bulletin of Engineering Tome VI (Year 2013) ISSN 2067-3809* (2013).