Int. J. Electrochem. Sci., 5 **(2010)** 774 - 781

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Electrochemical Investigations of Dopamine at Chemically Modified Losartan Carbon Paste Electrode: A Cyclic Voltammetric Study

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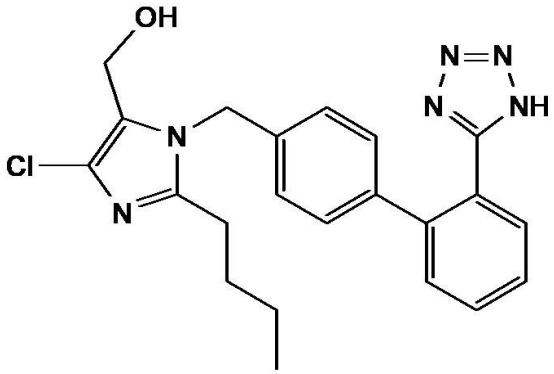
Received: 20 May 2010 / *Accepted:* 12 June 2010 / *Published:* 20 June 2010

A carbon paste electrode modified by Losartan was used for detection of dopamine (DA). The modified electrode exhibited strong promoting effect and stability towards the electrochemical oxidation of DA in phosphate buffer solution (PBS) at pH 7.0. The effects of scan rate, concentration, and pH have been studied. The detection limit of the modified carbon paste electrode was 1 x 10^{-7} M for dopamine. The preparation of the modified electrode is very easy and renewed by simple polishing gave very good reproducibility, high stability in its voltammetric response and low detection limit for DA.

Keywords: carbon paste electrode, losartan, dopamine, electrochemical oxidation, cyclic voltammetry.

1. INTRODUCTION

Losartan, (2-butyl-4-chloro-1-{[2'-(1H-tetrazol-5-yl) biphenyl-4-yl]- methyl}-1H-imidazol-5-yl)methanol [1] was the first of a new class of orally active, non-peptide angiotensin II (type AT1) receptor antagonists for the treatment of hypertension. Losartan (scheme.1) is a selective, competitive Angiotensin II receptor type 1 (AT_1) receptor antagonist, reducing the end organ responses to angiotensin II. [2–4]. Losartan may also delay progression of diabetic nephropathy and is also indicated for the reduction of renal disease progression in patients with type 2 diabetes, hypertension and microalbuminuria (>30 mg/24 hours) or proteinuria (>900 mg/24 hours).



Scheme 1. Structure of Losartan.

DA was discovered in the year 1950. It is one of the most important neurotransmitters and plays a significant role in the functioning of central nervous, renal and hormonal system as well in drug addiction and Parkinson's disease [5-6]. Therefore it is significant to develop sensitive and simple methods for the determination of dopamine. Methods for the detection of DA include chemiluminescence [7], fluorometry [8], ultraviolet spectroscopy [9], capillary electrophoresis [10], high performance liquid chromatography (HPLC) [11], and ion chromatography [12]. Since DA is electrochemically active compound it can also be determined by electrochemical methods [13-14].

One of the most common routes is to use a modified carbon paste electrode which has the ability to eliminate the interfering substances from DA determination. The study of electrochemical determination of DA with different modified electrode was reported [15]. The modification can be done by adding different types of modifiers. The modifier used for this work, the determination of electrochemical response of DA is Losartan.

The aim of the work is to establish a simple and sensitive electrochemical method for the determination of dopamine at modified Losartan carbon paste electrode. The oxidation peak current of dopamine remarkably increases at the Losartan modified carbon paste electrode suggesting significant improvement of determining sensitivity. Related works have been done by our research group [16-19]. The newly proposed work has advantages including high sensitivity, extreme simplicity, rapid response and low cost.

2. EXPERIMENTAL PART

2.1. Reagents and Chemicals

Losartan obtained as a gift sample from Jublient Organics. Dopamine hydrochloride and potassium ferrocyanide was purchased from Himedia. Dopamine was dissolved using 0.1 M perchloric acid ($HClO_4$). All other Chemicals were of analytical grade quality and were used without further purification. The water used was a double distilled in all the measurements. Phosphate Buffer [0.2 M] was prepared by 0.2 M disodium hydrogen phosphate and 0.2 M sodium dihydrogen phosphate.

2.2. Apparatus

The electrochemical experiments were carried out using a Model-201 Electroanalyser [EA-201 Chemilink system]. All the experiments were carried out in a conventional three electrode system. The electrode system contained a working carbon paste electrode (home made cavity of 3 mm diameter), a platinum wire as counter electrode and saturated calomel electrode as reference electrode.

2.3. Preparation of Losartan modified carbon paste electrode

Losartan Modified Paste Electrode (LMCPE) was prepared by grinding the different ratio's of losartan with 70 % graphite powder of 50 mm particle size of graphite powder and 30 % silicon oil in an agate mortar by hand mixing for about 30 minute to get homogeneous losartan modified carbon paste electrode. The paste was packed into the cavity of home made CPE of 3mm in diameter and smoothened on weighing paper. Similarly the BCPE was prepared without adding modifier.

3. RESULTS AND DISCUSSION

3.1. Electrochemical response of $K_4[Fe(CN)_6]$ *at a LMCPE*

To check whether LMCPE shows electrocatalytic properties for potassium ferrocyanide, The electrochemical response of $K_4[Fe(CN)_6]$ at a LMCPE was recorded and shown in Fig.1.

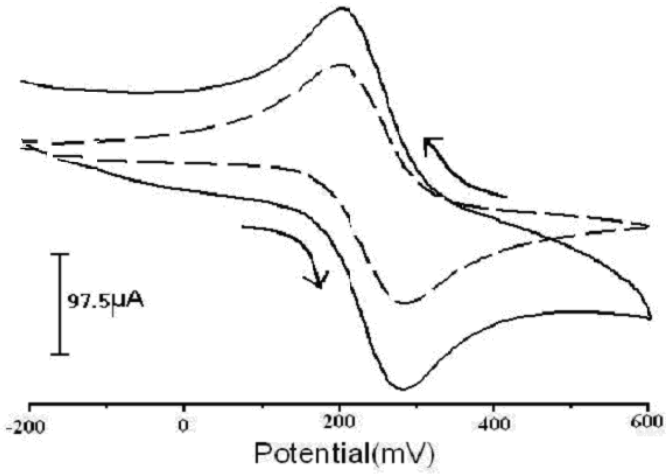


Figure 1. Cyclic voltammogram for 1mM $K_4[Fe(CN)_6]$at BCPE (dashed line) and LMCPE (solid line), at 50 mVs^{-1}.

At bare carbon paste electrode (BCPE) the voltammogram of $K_4[Fe(CN)_6]$ showed electrochemical response (dashed line) with irreversible behavior in 1 M KCl as supporting electrolyte.

However, the voltammetric response was improved at LMCPE (solid line) with decreasing the ΔEp. At BCPE the anodic peak potential (Epa) was found to be 280 mV and cathodic peak potential (Epc) 190 mV (vs. SCE). The separation of redox potential peaks (ΔEp) 80 mV and the ratio of peak current (Ipa/Ipc) was 1.5. At LMCPE, a pair of redox peak is obtained with strong increase in both anodic cathodic peak current. The Epa was found at 260 mV and Epc at 200 mV. The separation of redox potential peaks ΔEp was found to be 60 mV and the Ipa/Ipc was 1.03.

3.2. Effect of Losartan as modifier for investigation of DA

As the quantity of Losartan increases from 1mg to 20 mg, the current signal was increased upto 15 mg for 50 µM DA in 0.2 M phosphate buffer solution of pH 7.0, and further decreased by increasing the quantity of modifier. The graph of peak current vs. quantity of Losartan was plotted showed in Fig. 2.

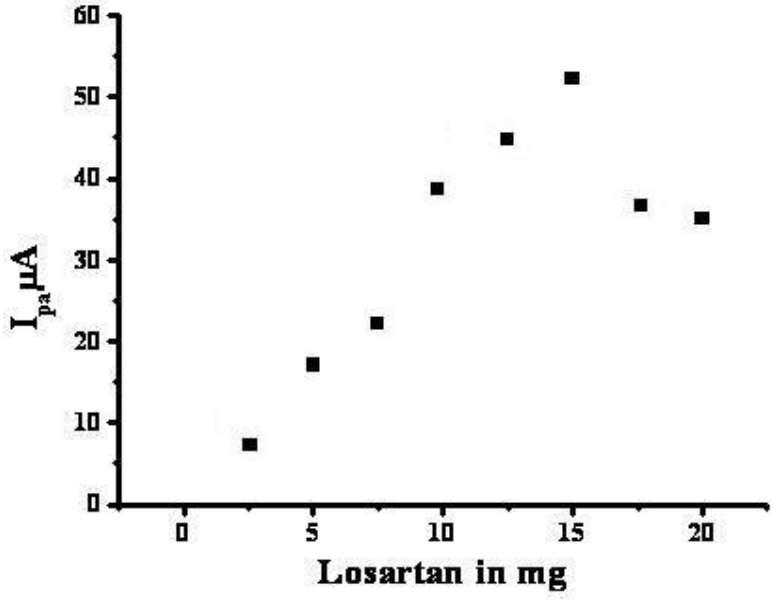


Figure 2. Graph of Ipa of DA vs different quantity of Losartan in carbon paste electrode.

Maximum current signal enhancement in 15 mg LMCPE and then gradually decreased for 20 mg LMCPE. However, better and acceptable voltammogram was obtained in 2 mg LMCPE, hence this ratio used for the study of all other parameters.

3.3 The electrochemical response of Dopamine at Losartan Modified Carbon paste electrode

Fig.3. shows the electrochemical response of 50µ M DA at BCPE and LMCPE in the presence of 0.2 M phosphate buffer solution in pH 7.0. The dotted line shows the electrochemical response of

DA at BCPE having the cathodic peak potential (Epc) 170 mV and anodic peak potential (Epa) 219 mV with poor current signals. The LMCPE shows in solid line the current enhancement of both electrochemical anodic and cathodic peak currents.

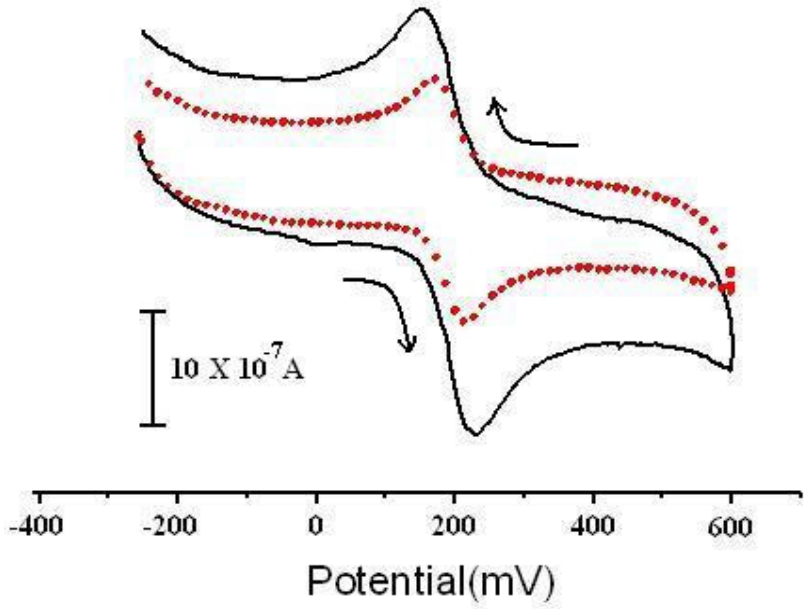


Figure 3. Cyclic voltammogram of 50µM DA in 0.2M phosphate buffer solution at pH 7 at BCPE (dotted line) and LMCPE (solid line), at 100mVs^{-1}.

The obtained voltammogram at LMCPE showed their anodic and cathodic peak potentials at 230 mV and 160 mV respectively. The ΔEp was found to be 70 mV. The enhancement in redox peak currents suggested the electrocatalytic property of LMCPE towards the DA detection.

3.4 Effect of Scan rate

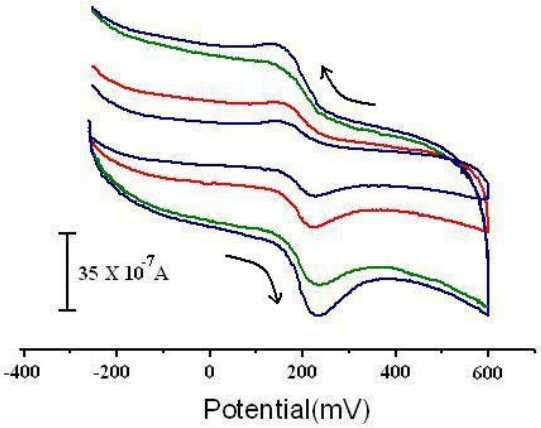
According to Randles-sevick's equation increase in the scan rate increases the peak current. The LMCPE showed increase in the peak current with increase in scan rate (50 mV/s to 250 mV/s) in 50 µM dopamine in 0.2 M phosphate buffer solution at pH 7.0.

Cyclic voltammogram for dopamine at LMCPE shown in Fig.4a. The graph of current Ipa vs. scan rate (υ) and square root of scan rate ($\upsilon^{1/2}$) were plotted as shown in Fig.4b.and Fig.4c respectively. In the range from 50 mV/s to 250 mV/s the anodic peak currents were proportional to the scan rate (υ) and also to the square root of scan rate ($\upsilon^{1/2}$) with correlation coefficient 0.9934 and 0.9843 respectively.

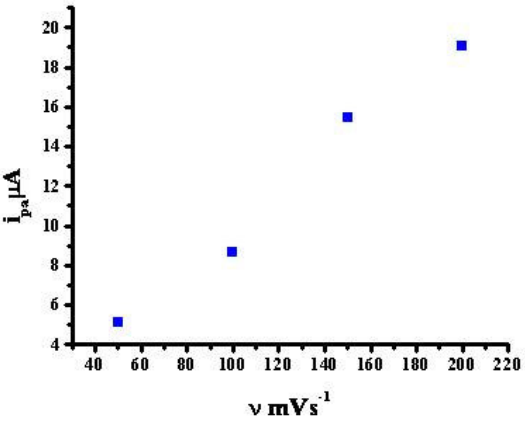
This indicates that, the electron transfer process was both adsorption controlled as well as diffusion controlled.

3.5 Effect of DA concentration

The electrocatalytic oxidation of DA was carried out by varying the concentration at LMCPE (Fig.5a). By increasing the concentration of DA from 50 µM to 250 µM, the Ipa and Ipc goes on increasing with negligible shifting Epa and Epc



4a



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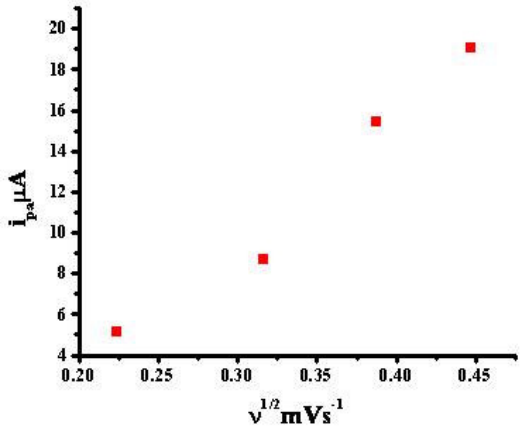

4c

Figure 4a. Cyclic voltammogram of 50µM DA at different scan rate (a-e; 50 mVs^{-1}, 100 mVs^{-1}, 150 mVs^{-1}, 200 mVs^{-1}, 250 mVs^{-1}) at LMCPE.
Figure 4b. Graph of current vs scan rate of DA.
Figure 4c. Graph of current vs square root of scan rate of DA.

The graph of Ipa vs concentration of DA was plotted, showed increase in electrochemical peak current, (Fig. 5b). The graph obtained linearly increase in peak current with increase in the DA concentration and Ipa is proportional to concentration of DA.

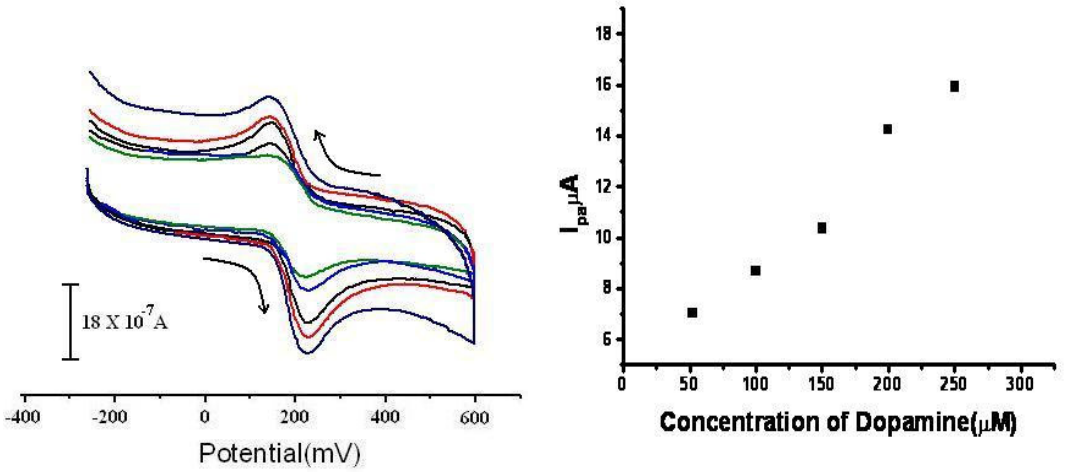

Figure 5a. Cyclic voltammogram for different concentration of DA (a) 50µM, (b) 100 µM, (c) 150µM, (d) 200µM and (e) 250µM at LMCPE with scan rate 100mVs^{-1}.
Figure 5b. Graph of current vs concentration of DA.

3.6 Effect of pH

The effect of variation of pH was studied for 50 µM DA in the range from 2.0 to 9.0 using 0.2 M phosphate buffer as a supporting electrolyte at a scan rate of 100 mV/s at LMCPE. The electrochemical response of DA at LMCPE is generally pH dependent. The both anodic and cathodic peak potentials were shifted to less positive side with increasing in the pH values. The anodic peak potential of DA shifted from 530 mV to 165 mV with respect to the pH from 2 to 9. The potential diagram was constructed by plotting the graph of calculated E^0 vs pH of the solution (fig. 6). The graph has good linearity with a slope of 51 mV/ pH, this behavior is nearly obeyed the Nernst Equation for two electron and two proton transfer reaction.

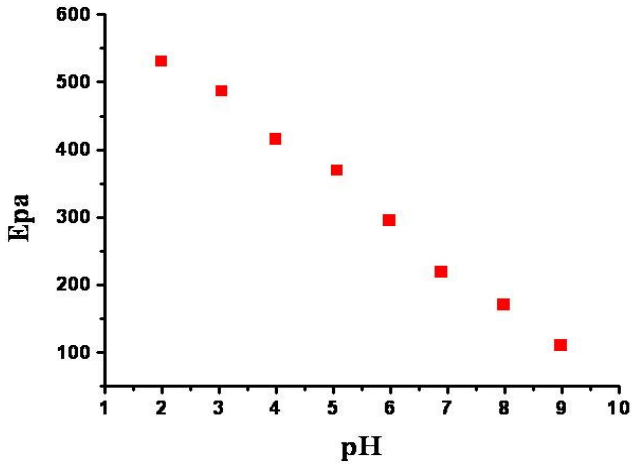

Figure 6. Graph of E^0vs pH

4. CONCLUSION

In this work, the Losartan modified carbon paste electrode was able to show high sensitivity for voltammetric detection of dopamine. The high sensitivity, easy preparation, surface regeneration of the modified electrode and the reproducibility of the voltammetric response make the prepared modified system very useful in the construction of simple devices for the determination of dopamine in clinical and pharmaceutical preparations. The modified electrode acts as good sensor for dopamine and can be further applied for the investigation of other neurotransmitter.

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