Poly(Methyl Red) Modified Glassy Carbon Electrode As A Voltammetric Sensor For The Sensitive And Cost Effective Determination Of L-DOPA

Sonia Sam and K. Girish Kumar*
soniasam13@cusat.ac.in, *giri@cusat.ac.in
Department of Applied Chemistry, Cochin University of Science and Technology, Kochi-22

Abstract:

L-3, 4-dihydroxyphenylalanine (L-dopa) is an amino acid and a precursor to many neurotransmitters. It mediates the neurotropic factor release by the brain and is used for the treatment of Parkinson's disease. In this point of view, Poly(methyl red) modified glassy carbon electrode(PMR/GCE) was fabricated for the determination of L-dopa. The modified electrode was characterized using Scanning Electron Microscopy. The PMR/GCE shows good electrocatalytic activity towards L-dopa and the anodic peak current was enhanced dramatically by about 5fold compared to bare electrode. The experimental parameters for the determination of L-dopa using developed sensor were optimized and it shows best results in 0.1 M PBS pH 6. A linear response was obtained over the concentration range 0.9 μM-10 μM using square wave voltammetric technique. This electrochemical sensor exhibited good response for accurate determination of L-dopa in artificial blood serum and urine samples.

Introduction

L-Dopa (L-3,4-dihydroxyphenylalanine) is a chemical substance that widely exists in animals and plants. However clinical data shows that L-Dopa is toxic in vivo when it is present in high concentrations.[1] Parkinson's disease (PD) is a neurodegenerative disease which is characterized pathologically by the lack of pigmented dopaminergic neurons. L-Dopa can be used in the treatment of PD as it can induce the production of Dopamine. It is the precursor to many other neurotransmitters too. Hence the monitoring of L-dopa in biological fluids is very important. In this context, a simple, sensitive and cost effective electrochemical sensor based on Poly(methylred) modified glassy carbon electrode(PMR/GCE) was fabricated for the detection and determination of L-dopa.

EXPERIMENTAL

Apparatus.-Electrochemical studies were performed by an electrochemical analyser(CH instruments, USA).The fabricated PMR/GCE, platinum wire and Ag/AgCl electrodes were employed as working, auxillary and reference electrodes respectively.The solution in the cell was purged with nitrogen before every measurements and were made under unstirred conditions at room temperature.

Chemicals.-Methyl red and L-Dopa were purchased from s.d.fine chemicals,India and spectrochem Pvt Ltd,India respectively.All the chemicals used are of analytical grade.

Fabrication of PMR/GCE.-Intially the electrode was cleaned and dried in air.After that,electropolymerization of methyl red was performed in 0.5M NaNO3solution containing 1mM methyl red by cycling potential between -1.0 to 2.2V at a scan rate 0.1V/s for 25 cycles.[9]

Analytical Procedure.-Desired volume of L-Dopa was pipetted out into an electrochemical cell containing 0.1M PBS and square wave voltammetric measurements were recorded from 0.0 to 1.0V at a scan rate of 0.1V/s with pulse amplitude 0.025V, increment 0.004V and frequency 15Hz using PMR/GCE as the working electrode.

RESULTS AND DISCUSSION

Optimization of experimental parameters

All the experimental parameters such as number of cycles of polymerisation, effect of supporting electrolyte and its pH, were optimized for the effective electrooxidation of L dopa on PMR/GCE.

As the number of cycles of polymerisation is directly proportional to the thickness of the polymer film, it was optimized and found that 10 cycles of polymerisation of PMR on GCE gave better results.

The electrochemical response of L-dopa on PMR/GCE was studied in different supporting electrolytes such as Acetate buffer solution (ABS), Phosphate buffer solution (PBS), Citrate buffer solution (CBS), NaOH, KCl, HCl, H_2SO_4 and NaCl solutions. Better response was obtained for 0.1M PBS of pH 6.

Probing L-dopa on modified electrode surface

On bare GCE, 1×10^{-4} M L-Dopa gets electroxidised at a potential 0.244V with an anodic peak current 4.29×10^{-6}A, and for modified GCE more than 4fold increment in peak current (Ip=1.897×10^{-5}V) at 10256V was optained(Fig.1). This confirms that the polymer film act as an efficient catalyst in the electrochemical oxidation of L-Dopa on GCE.

Under optimized conditions the sensor was found to be useful for the quantification of L-Dopa in the range 1.00×10^{-5}M to 9.00×10^{-7}M (Fig.2). The limit of detection was found to be 6.6×10^{-7}M.

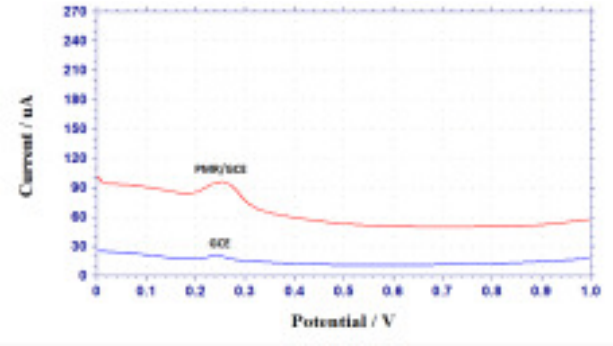


Fig:1 Overlay of SWV plots for the elecroxidation of 1 $\times10^{-4}$ L-Dopa on bare and modified GCE

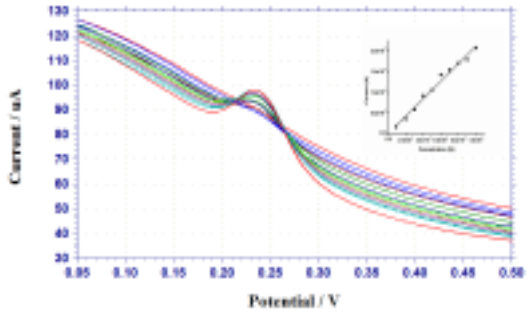


Fig:2 Overlay of SWV plots for the electrooxidation of L-Dopa on PMR/GCE in the concentration range 1×10^{-5} to 9×10^{-7}.Inset:Calibration curve of L-Dopa in the corresponding linear range.

Mechanistic study of the electrochemical process

At PMR/GCE 1×10^{-4}M L-Dopa gave a cyclic voltommagram with anodic peak at Epa=0.2775V and cathodic peak at Epc=0.2385V.Therefore a perfectly reversible oxidation of l-Dopa is revealed from 0.039V separation between Epa and Epc.Moreover the number of electrons involved in the electro-oxidation is calculated to be 2.(E=0.059/no.of electrons).Also the scan rate studies shows that the electrochemical oxidation of L-Dopa is diffusion controlled.Thus the possible mechanism is given in scheme A.



Scheme A. Mechanism of electro-oxidation of L-Dopa

Application study

The performance of the sensor in physiological samples such as artificial blood serum and urine were evaluated and the results are tabulated to examine its practical utility(Table 2)

Table 2: **Application study**

Samples	Added(M)	Found(M)	Recovery(%)
Artificial blood serum	4×10^{-6} to 1×10^{-5}	4.189×10^{-6} to 0.999×10^{-5}	101.6319
Artificial urine	3×10^{-6} to 7×10^{-6}	3.096×10^{-6} to 6.959×10^{-6}	97.0419

CONCLUSION

A sensitive, reliable and selective voltammetric technique for the determination of L-dopa based on the electrochemical oxidation of it on PMR/GCE have been developed. The oxidation peak current showed a linear range from 1.00×10^{-5} to 9.00×10^{-7} M with a detection limit 6.6×10^{-7}. The utility of the developed sensor was assessed in artificial blood serum and urine samples.

ACKNOWLEDGEMENT

The author Sonia Sam would like to acknowledge Council of Scientific and Industrial Research for financial assistance in the form of Junior Research Fellowship.

REFERENCES

1. L. Lin, H. Lian, X. wun, Y. Yu, B. Liu, *Anal. Methods*, **2015,** *1387*, **7**
2. H. Yao, Y. Sun, X. Lin, Y. Tang, L. Huang, *Electrochem. Acta*, , 2007, *6165*, **52**.
3. W. Yazhen, Q. Hongxin, H. Siqian, X. Junhui, *Sens. Actuators*, B, 2010, *587*, **147**.
4. T. Arfin, S. N. Rangari, *Anal. Methods*, 2018, *347*, **10**.
5. H. Wang, Y. Chen, N. li, Y. Liu, *Michrochim.Acta*, 2017, *515*, **184.**
6. R. S. Aparna, J. S. Anjlali Devi, N. John, K. Abha, S. S. Syamchand, S. George, *Spectrochim. Acta, A, Mol. Biomol. Spectrosc*., 2018, *123*, **199**.
7. Q. Zhang,C. Wang, Y. Lv, *Analyst*, 2018, *4221*, **143**.
8. H. Dong, W. Gao, F. Yan, H. Ji, H. Ju, *Anal.Chem*., 2010, *5511*, **82**.
9. K. Huang, C. xu, W. Xie, *Bull. Korean Chem.Soc*., 2008, *988*, **29**.
10. D. Kul, G. Ozturk, *Electroanalysis*, 2017, *1*, **29**.
11. Y. Zhou, M. He, S. Dong, J. Zheng, *J. Electrochem. Soc*., 2012, *F17*, **159**.
12. T. E. Chiwunze, V. K. Palakollu, A. S. Atal, F. Kayamba, N. B.Thapliyal, R. Karpoormath, *Mater. Sci. Eng. C*, 2019, *97*, **285**.
13. M. D. Imisides, R. John, P. J. Riley, G. G. Wallace, *Electroanalysis*, 1991, *879*, **3**.