DEVELOPMENT OF ELECTROACTIVE POLYMETHYLTHIOPHENE BASED DOPAMINE SENSOR

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Abstract

Electrodes modified by the electroactive conductive poly(3-methylthiophene) (PMeT) were investigated as chemical sensors for voltammetric analysis of dopamine. The electrochemical behaviors of dopamine was examined by differential pulse voltammetry. Voltammetric responses were affected by the nature of the electrolyte and its pH. Also, the effect of increasing film thickness enhanced of reduction peak height. Furthermore, the selective responses towards dopamine of the PMeT/Nafion modified electrode improve significantly in comparison with PMeT modified electrode, showing in the linear range from 1 to 200 μM in 0.1 M H_2SO_4 a slope of 0.839 μA/μM against 0.201 μA/μM, respectively.

Keywords: conducting polymer, dopamine, electrochemical, Nafion, polymethylthiophene.

1. Introduction

As a neurotransmitter, dopamine (DA) plays an important role in the activity of central and peripheral nervous systems. A loss of DA containing neurons may result in serious diseases such as Parkinsonism and schizophrenia [2]. The most widely used methods for determination of this biogenic amine are fluorometric, radioenzymatic, HPLC and voltammetric assays [1,12].

In the last two decades, the need for highly sensitive and selective analysis of single bio-molecules has been increasing. Poly(3-methylthiophene) (PMeT), polypyrrole (PPy) and polyaniline (PAni) are electronically conducting polymers which are easily deposited onto electrodes by the electrooxidation of their monomers. The electrode materials most commonly used in amperometric systems are glassy carbon, platinum and gold electrodes. The performance of these electrode materials depend mainly on the method and quality of surface polishing and pretreatment [1,10]. Recently, electroanalysis using chemically modified electrode surface has gained extensive attention among analytical chemists and others. The properties of the coated materials onto the substrate are deliberately designed to enhance the sensitivity and the selectivity of the measurement.

In this study we examine the electrochemical behavior of dopamine on PMeT modified platinum and glassy carbon electrodes. Effects of conducting polymer film, the nature of the supporting electrolyte and pH are also studied.

2. Experimental

2.1. Reagents

3-methylthiophene (MeT) purchased from Fluka (Switzerland) is used without further purification. Tetrabutylammonium tetrafluoroborate (TBATFB) and dopamine hydrochloride are from Sigma (Germany). Nafion 0.5% solution in ethanol is prepared from Nafion® 117 solution (Fluka, Switzerland). Other chemicals are from Merck (Germany). All aqueous solutions are prepared with Milli-Q water. Phosphate buffer solutions are prepared from disodium hydrogenphosphate, sodium dihydrogenphosphate and phosphoric acid.

2.2. Apparatus

Electropolymerization is carried out with a 757 VA Computrace electrochemical analyzer (Metrohm, Switzerland), in a three electrode cell consisting of a Ag/AgCl (NaCl 3M) reference electrode and a platinum rod auxiliary electrode (Metrohm, Switzerland), the working electrode can be a platinum disk

electrode (Bioanalytical Systems, USA) or a glassy carbon (GCE) disk electrode (2 mm i.d., Metrohm, Switzerland). pH measurements are carried out with a pH-meter 744 (Metrohm, Switzerland).

2.3. Electrode preparation

The Pt and GC electrodes are polished with alumina slurry (0.05 µm), washed with Milli-Q water and finally in a water-filled ultrasonic bath for 30 s. The GCE is subsequently subjected to cyclic voltammetry in 1.0 M sulfuric acid between -0.1 and +1.6 V with a rate of 100 mV/s for 5 cycles, washed and allowed to dry at room temperature in dessicator.

Electrochemical polymerization is carried out in a one compartment cell containing a nitrogen-purged solution of 100 mM TBATFB and 150 mM MeT in acetonitrile. The polymer films were grown for 20 s at a constant potential of 1.8 V vs. Ag/AgCl with Pt electrode and 1.75 V with GC electrode.

Preparation of Nafion-doped PMeT-coated electrodes require an additional step prior to polymerization. 5 µl of Nafion 0.5% solution are carefully deposited on the electrode surface using a 25-µl syringe (SGE, Autralia) then the solvent is allowed to evaporate at 45 °C in oven for 5 min to create a thin film.

3. Results and discussion

3.1. Effect of pH and electrolyte

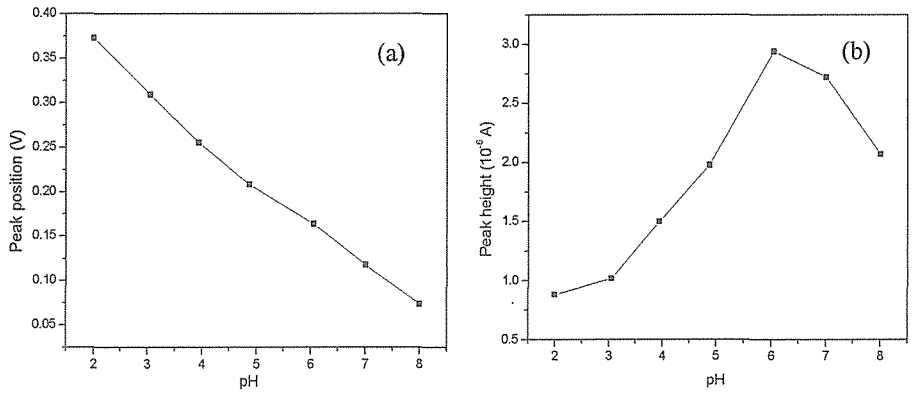

Fig. 1. Effect of pH value of PBS on peak position (a) and peak height (b) of 0.5 mM dopamine at Pt/PMeT electrode.

PBS pH 7 is a common buffer solution for electrochemical analysis of biogenic compounds such as dopamine, providing a pH similar to that of physiological samples. In this study it is demonstrated that at pH 6.0 dopamine gives the highest response in DPV (Fig. 1a). Additionally, the reduction peak shifts to lower potentials with increasing pH values (Fig. 1b). However, analysis of real samples will be more complicated because peak position and height also depends on the electrolyte content of the solution (Table 1). Although PBS and 0.1 M sulfuric acid allow similar performance in term of amplitude of the signal, the dynamic range with PBS is limited to 80 µM while the response curve with sulfuric acid is linear up to 200 µM (Fig. 2). In acidic media, the reduction peak of DA shift to higher potentials.

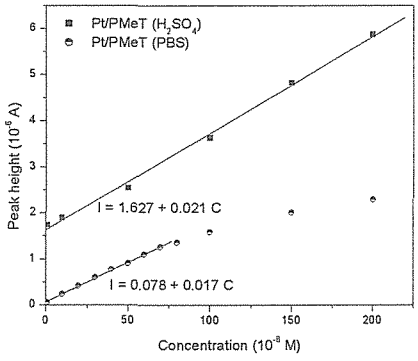

Fig. 2. DPV response to dopamine in PBS and H_2SO_4

Table 1. Effect of electrolyte type on the anodic peak potential and current of 1mM dopamine at Pt/PMeT electrode

Electrolyte (0.1 M)	Position (V)	Height (μA)
PBS (pH 7)	0.161	7.76
H_2SO_4	0.429	6.12
Na_2SO_4	0.257	3.64
HCl	0.414	2.41
NaCl	0.28	2.59
$NaNO_3$	0.289	2.72
NaF	0.217	5.7
$NaCH_3COO$	0.156	5.8

3.2. Effect of the thickness of the electron-transfer polymer layer

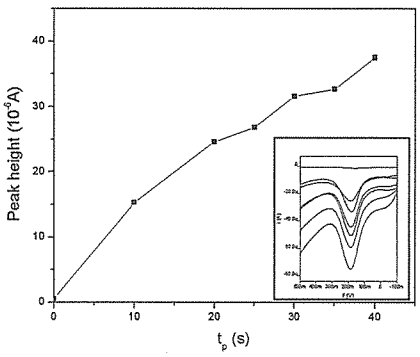

Fig 3. Effect of PMeT film thickness on the response with 5 mM dopamine. Scan rate: 4 mV/s, pulse: 25 mV in PBS.

Thicker conducting polymer films are known to allow better electron transfer at the expense of their mechanical robustness [1]. In our case, the cathodic peak height is enhanced with increasing polymerization time (Fig. 3). However, the shape of the DPV curve also becomes deformed which would make quantification more difficult. For all further experiments, a polymerization time of 20 s is chosen as compromise between high amplitude and good shape of the signal.

3.3. Effect of Nafion doping of the PMeT film

At pH values less than 7, DA exists predominantly in the cationic form ($pK_{a,DA}$ = 8.93) [8]. As such, the signal of DA can be enhanced by improving the cation exchange capacity of the conducting polymer layer. Various studies have shown that the presence of a bulky anion dopant in a solid contact layer such as conducting polymer is beneficial for the cation exchange capacity of this layer: dodecylsulfate and Nafion have been commonly used for polypyrrole-based solid contact ion selective electrodes for cations such as hydrogen, potassium and ammonium [5,6]. In another approach, poly(styrene sulfonic acide) in conjunction with carbon nanotubes for determination of dopamine has also been reported [9]. In this study, possible enhancements by addition of Nafion in the PMeT matrix is investigated.

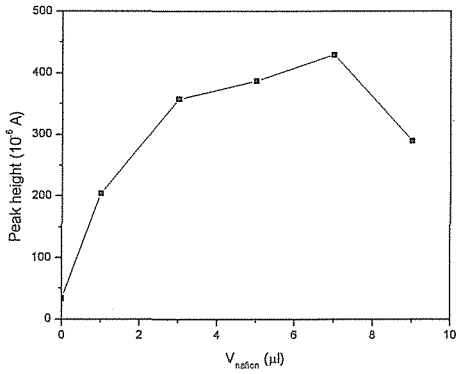

Fig. 4. Effect of the Nafion doped PMeT with a volume of Nafion from 0 µl to 9 µl.

Addition of Nafion to the PMeT layer improves indeed the signal of DA (Fig. 4). Also, the degree of improvement depends on the amount of Nafion. Higher peaks of DA are found with larger volume of Nafion deposited which indicates an increase in cation exchange of the PMeT layer. However, the signal decreases if the volume of Nafion is larger than 7 µl which might be due to deterioration of the conductive properties of PMeT by structural alteration.

3.4. Separation of DPV peaks of dopamine and ascorbic acid

Determination of dopamine in physiological samples by DPV using bare electrode is impossible due to strong interference from ascorbic acid (AA). DA and AA have similar reduction potentials at bare GCE [4] and the two respective signals overlap. Moreover, the concentration of AA *in vivo* is usually higher than that of DA by 2–3 orders of magnitude [11]. By using PMeT-modified electrodes, the two signals can be better separated but AA still interferes significantly at higher concentrations (Fig. 5a). Compared to the PMeT electrode, PMeT/Nafion electrode permits superior separation by shifting the AA peak even further to the lower potential. The DPV curves of a mixture of DA and AA at GC/PMeT/Nafion electrode in H_2SO_4 0.1 M (Fig. 5b) show peaks of DA and AA at respectively 0.45 and 0.21 V, thus the difference in oxidation potentials is 240 mV. The DA peak current decreases with greater AA concentration but only slightly. Increasing AA concentration from 1 to 10 mM causes the peak current of 10 µM DA to drop by approximately 12%, from 18.1 to 15.9 µA.

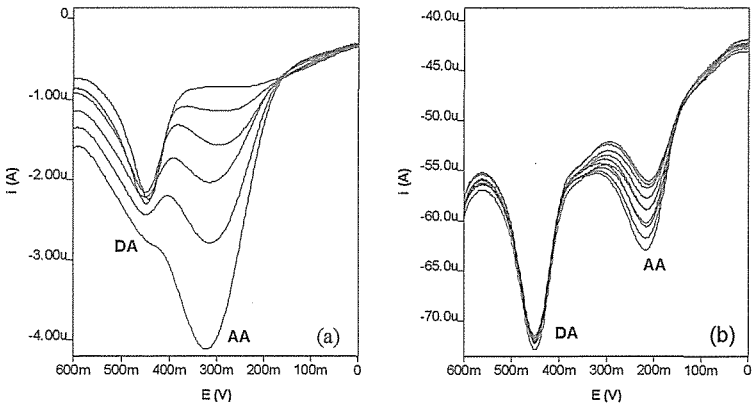

Fig. 5. DPV curves of (a) GC/PMeT electrode in 100 µM DA + 0–4 mM AA and (b) GC/PMeT/Nafion electrode in 10 µM DA + 0–10 mM AA.

3.5. Dynamic voltammetry responses of dopamine at conducting polymer electrodes

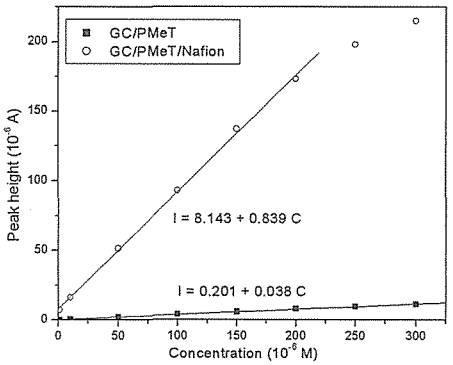

Fig. 6. The calibration curves for dopamine at GC/PMeT and GC/PMeT/Nafion electrodes. Scan rate: 4 mV/s, pulse: 25mV in H_2SO_4

Fig. 6 depicts the voltammetric response of DA with different concentrations at PMeT and Nafion/PMeT modified electrode in 0.1M H_2SO_4. It should be found that the response of DA at Nafion/PMeT higher at PMeT modified electrode. The voltammetric response of dopamine at the PMeT/Nafion electrode shows linearity from 1 to 200 μM with a slope of 0.839 μA/μM (n = 4).

4. Conclusions

In this work, we compared the electrochemical behavior of dopamine at polymethylthiophene and polymethylthiophene/Nafion modified electrodes. Prepared under similar conditions, both PMeT and PMeT/Nafion films are improvement over bare electrodes in term of signal amplitude and signal separation with ascorbic acid. PMeT/Nafion modified electrodes show superior characteristics over PMeT, with 4 fold sensitivity improvement (0.839 against 0.201 μA/μM) and good selectivity over ascorbic acid. For electrolytic conditions of the measurement, H_2SO_4 is found to provide better responses than the more commonly used phosphate buffer.

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