Selective Electrochemical Sensor Using Screen-Printed Carbon Electrode (SPCE) for Dopamine Detection in Neutral Condition

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A selective electrochemical sensor for detecting dopamine (DA) has been studied using a screen-printed carbon electrode (SPCE). The performance of SPCE was characterized using cyclic voltammetry at pH 7.0 in 0.1 M phosphate buffer solution. The measurement was done in a potential range of -7.5 to 1 V at room temperature. The effect of DA concentration and scan rate was observed. The result showed that DA can be detected specifically by looking at its reduction peak signal at a potential of -0.11 V, $i_{pc} = -52.13$ µA. The signal of DA was monitored without any interference signals from ascorbic acid, glucose, uric acid, paracetamol, and urea. The obtained calibration curve, which represents various concentrations of DA as a function of peak current, followed the linear equation $i_{pa} = 3.484 + 0.413x$ with $R^2 = 0.992$ and $i_{pc} = -2.741 - 0.267x$ with $R^2 = 0.985$. The limits of detection and sensitivity of SPCE for DA detection were 0.030 µM and 8.107 µA·mm^{-2}·µM^{-1}, respectively. The effect of scan rate demonstrated a diffusion-controlled behavior from the reaction between SPCE and DA. The repeatability study of SPCE showed an increase in the peak current value. This is due to DA poisoning, resulting in less precision of repeated measurements.

Keywords: Dopamine (DA), SPCE, Voltammetry, Neutral condition.

1. INTRODUCTION

Dopamine (DA) is one of the natural catecholamines that play an important role as neurotransmitters in the hormone system, the nervous system of the cardiovascular and central nervous system [1, 2]. In the human body, DA is found in the arcuate nucleus in the brain's hypothalamus [3]. The normal range of DA in the human body is 0.01 to 1 µmol/l [4]. A low level of DA can cause some diseases, i.e., Alzheimer, Parkinson, Schizophrenia [3], and HIV infection [5]. Therefore, the accurate detection of DA in the biological fluids is important.

An electrochemical sensor is commonly used for detecting a biochemical compound such as DA [2, 6]. This method is relatively fast, simple, easy to use, and low-cost. Furthermore, the electrochemical sensor is the best choice for DA quantitative detection because of it is an easily oxidizable compound. The electrochemical sensor is mostly fabricated by modifying the electrodes with specific materials to improve selectivity and sensitivity. The specific materials for electrode modification that have been reported are gold nanoparticles [3], nanoparticles of NiCo/Ni [7], carbon nanoparticles [8], [9], and SWCNT/KB/AuNPs/GCE [10]. However, a significant problem for the electrochemical sensor of DA detection arises in interference ascorbic acid and uric acid. It is due to ascorbic acid and uric acid can be oxidized at nearly of similar potentials as DA [11].

In this work, we used the electrochemical sensor based on Screen Printed Carbon Electrode (SPCE) for DA detection. SPCE has a high selective to the target compound without any interferences [12-14]. The performance of SPCE for DA detection was evaluated using cyclic voltammetry (CV) at pH 7 in 0.1 M phosphate buffer solution at room temperature. The interference study was conducted in the presence of ascorbic acid, uric acid, glucose, paracetamol, and urea. The performance of the SPCE was compared with other work.

2. EXPERIMENTAL

The Screen-Printed Carbon Electrode (SPCE) was purchased from POTEN. Dopamine [$C_8H_{11}NO_2$, 98 %], uric acid [$C_5H_4N_4O_3$, 99 %] were purchased from sigma Aldrich. L(+)-Ascorbic acid [$C_6H_8O_6$], D(+)-Glucose [$C_6H_{12}O_6$], and urea [$CO(NH_2)_2$ 99.5 %] were purchased from Merck. Paracetamol [$C_8H_9NO_2$] was obtained from a local market. All chemicals were used without any purification. Phosphate buffer of 0.1 M (pH 7.0) was prepared in the Laboratory of Instrumentation and Analytical Sciences, Chemistry Department, Faculty of Science and Data Analytics, Institut Teknologi Sepuluh Nopember. Demineralized water was bought from a local market and used for cleaning and chemical preparation.
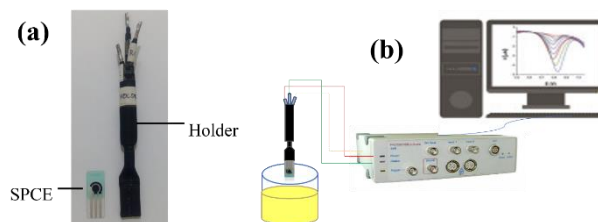

Fig. 1 – Photograph SPCE and holder (a) Schematic of an electrochemical apparatus circuit for a dopamine sensor using SPCE (b)

Electrochemical measurement was carried out using a potential from an electrochemical analyzer (mod-

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el700B, equipped with ALS/CHI700B software) and eDAQ (potentiostat E161 and e-coder 401, equipped with e-chem software version 2.1.13). (Fig. 1a) shows a photograph of SPCE and its holder. The electrochemical apparatus in this work is shown in (Fig. 1b).

Electrochemical experiments were performed by cyclic voltammetry (CV). The potential was swept from − 7.5 to 1 V. The scan rates were 25, 50, 100, 125 mVs⁻¹. The stock solutions were made by dissolving DA, ascorbic acid, glucose, uric acid, paracetamol, and urea in 0.1 M phosphate buffer solutions. The various of DA concentrations used to obtain the calibration curve were 0 μM, 2 μM, 4 μM, 6 μM, 8 μM, and 10 μM. The LOD and sensitivity of DA were determined using a linear calibration curve equation. The calibration curve was plotted from the maximum potential of anodic and cathodic peak current. The selectivity of SPCE was analyzed by measuring 10 mM of DA, ascorbic acid, glucose, uric acid, paracetamol, and urea solutions. The repeatability of the SPCE was tested toward 50 μM DA solution in 0.1 M phosphate buffer (pH = 7.0). The repeatability of the measurement was conducted for 5 cycles with 5 replications at 2 days in a row. The data of repeatability measurement was analyzed using significance testing. All experiments were performed at room temperature.

3. RESULTS AND DISSCUSION

The data obtained from electrochemical measurement was used to analyze the performance of SPCE for DA detection. The cyclic voltammogram from 0.1 M phosphate buffer solution (pH 7.0) with and without DA is shown in Fig. (2) The oxidation peak of DA appeared at + 0.236 V (i_{pa} = 10.235 μA). Furthermore, the reduction peak was found at + 0.002 V (i_{pc} = − 6.075 μA). Fig. 2 also shows that the process of oxidation reaction has higher peak current than the reduction reaction. It indicates that the SPCE can be applied for DA detection.
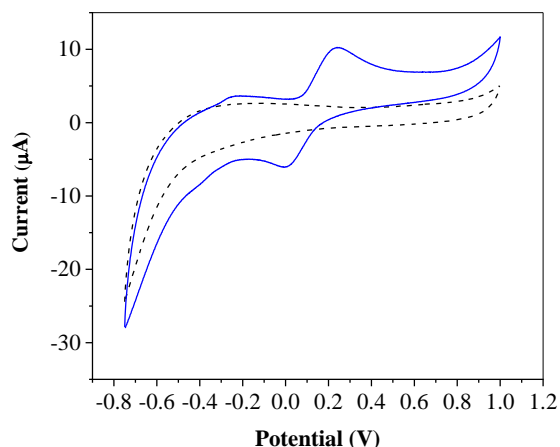

Fig. 2 – Cyclic voltammograms obtained for SPCE in 0.1 M phosphate buffer solution at pH 7.0 (black dash) and 30 μM DA in 0.1 M phosphate buffer solution at pH 7.0 (blue line), at a scan rate of 100 mVs⁻¹

The detection performance of SPCE was studied at different concentrations of DA. (Fig. 3a) shows that the anodic current peak increases with increasing DA concentrations. (Fig. 3b) shows the calibration curve obtained using an i_{pa} value of + 0.236 V. The linear regression equation and the correlation coefficient (R^2) are $i_{pa} = 3.484 + 0.413x$, with $R^2 = 0.992$, respectively. The calibration curve also was determined from ipc value of + 0.002 V with linear regression is $i_{pc} = − 2.741 − 0.267x$, with ($R^2 = 0.985$).
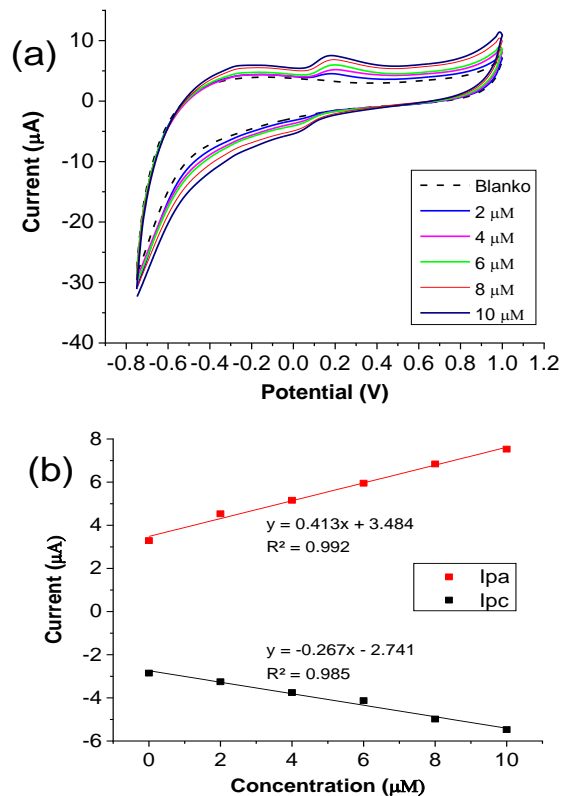

Fig. 3 – Cyclic voltammograms obtained for SPCE in various concentrations of DA (0, 2, 4, 6, 8, 10 μM) in 0.1 M phosphate buffer solution at pH 7.0, at scan rate of 100 mVs⁻¹ (a). Calibration curve of dopamine (b)

The limit of detection (LOD) is calculated using Eq. (1). The LOD is defined as the smallest concentration that can be detected by the electrode or sensor [15].

$$LOD = \frac{3S_b}{m},\qquad (1)$$

where S_b is the standard deviation of the blank signal and m is the slope of the calibration curve. The *LOD* of the SPCE for DA has been found to be 0.03 μM. Calculation using the linear regression equation in (Fig. 3b) shows that the sensitivity of the SPCE is 8.107 μA mm⁻² μM⁻¹. Comparison with the other electrodes indicates that the SPCE has a lower LOD Table 1. Therefore, the SPCE demonstrates as an alternative sensor for UA determination.

The effect of scan rates, which depend on the potential sweep rate, has been studied in order to assess whether the processes on the SPCE are controlled by diffusion or adsorption [19]. The cyclic voltammogram of SPCE in the presence of 50 μM DA at various scan rates is shown in (Fig. 4a). The scan rates shifted the E_{pa} slightly to more positive potentials and increased the peak current. (Fig. 4b) shows the peak current for the anodic oxidation that proportional to the square root of the scan rate according to the Randles-Sevcik equation Eq. (2) [20].

Table 1 – Comparison of SPCE performance with several electrodes

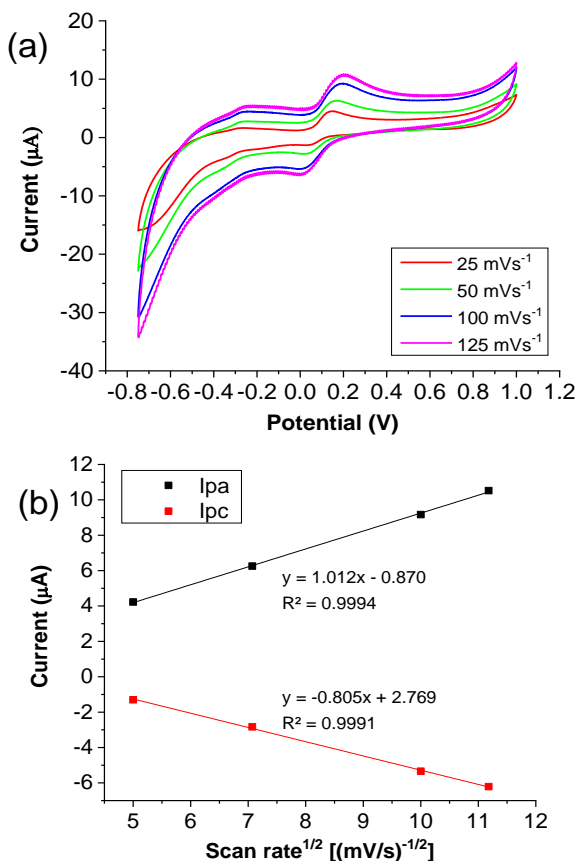| Electrodes	Linear range (µM)	*LOD* (µM)	Sensitivity (µA mm^{-2} µM^{-1})	References
HNP-AuAg alloy	5-335	0.20	–	[16]
PG/GCE	5-710	2.00	–	[17]
IDE/PEDOT-CNT-Ty-GAD-LFR	100-500	2.40	–	[6]
Tyrosinase/NiO/ITO	2-100	1.04	0.06	[18]
Modified nano-Au	4-40	2.00	–	[3]
Modified SWCNTs	1-10	0.79	3.41	[8]
SWCNT/KB/AuNPs/GCE	10-18	0.49	52.12	[10]
SPCE	2-10	0.03	8.107	This work

Fig. 4 – Cyclic voltammograms for 50 µM dopamine solution, in 0.1 M phosphate buffer solution at pH 7.0 using SPCE with different scan rate 25, 50, 100, 125 mVs^{-1} (a). Variation of current with the square root of scan rate (b)

$$(i_p = (2.69 \times 10^5)\, n^{3/2} AC\, D^{1/2}\, v^{1/2}, \qquad (2)$$

where i_p is the peak current, n is the number of electrons, A is the electrode area, C is the concentrations, D is the diffusion coefficient. The linear regression equation obtained for this relation is i_{pa} (µA) $= -0.870 + 1.012^{1/2}$ (mV$^{1/2}$s$^{-1/2}$) with $R^2 = 0.9994$ and i_{pc} (µA) $= 2.769 - 0.805v^{1/2}$(mV$^{1/2}$s$^{-1/2}$) with $R^2 = 0.9991$. The results show that the interaction between SPCE and dopamine solution is controlled by diffusion.

Repeatability of measurement for SPCE was carried out to determine the electrode stability when being tested repeatedly. A cyclic voltammogram of DA for both the first and second days is shown in (Fig. 5a) and (Fig. 5b), respectively. The repeatability of DA measurements using SPCE can be found in Table 2.
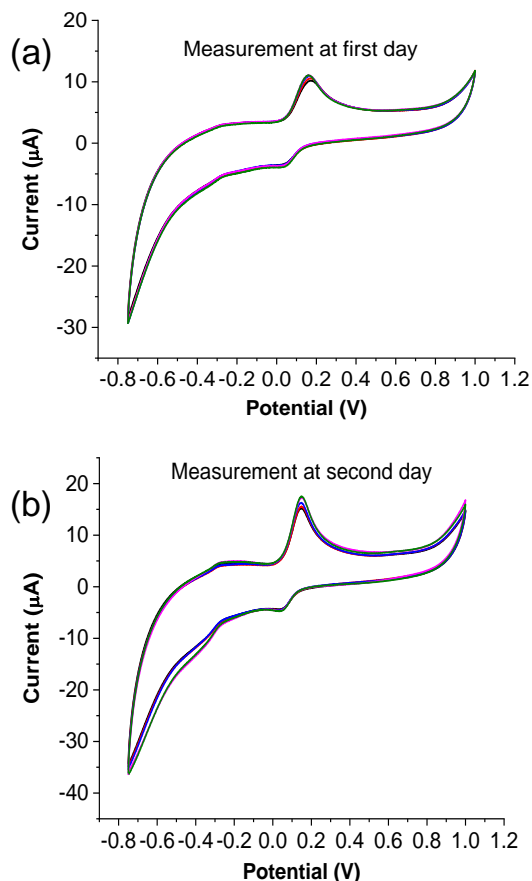

Fig. 5 – The first five cyclic voltammogram for 50 µM DA on the first day (a) on the second days (b), in 0.1 M phosphate buffer at pH 7.0 measurement by SPCE

The oxidation peak from the measurements has been analyzed using *F*-test and *t*-test. This shows that at the 95 % confidence level, the measurement data has precision on each measurement day. It can be concluded that Ho is accepted.

The results *F*-test on DA shows that the value of *F*-calculated is lower than the *F*-critical value (Table 3). After the *F*-test was carried out to see the precision of the test results on each measurement on the first and second days, then a *t*-test was carried out to see the significance of the test results on the first and second days. The results of the *t*-test Table 4 shows that the data of the oxidation current of dopamine solution with SPCE for the first-day measurement versus the second-day measurement resulted in the value of *t*-calculated is higher than *t*-critical value. It can be concluded that

Ho is rejected. Significant testing has proven that SPCE has poor performance when repeatedly used because there will be an increase in peak current values due to dopamine poisoning resulting in less precision of repeated measurements.

Table 2 – Repeatability of DA measurement using SPCE

Measurements	First day	Second days
1	10.229 μA	15.208 μA
2	10.592 μA	15.596 μA
3	10.938 μA	16.296 μA
4	11.121 μA	17.311 μA
5	11.103 μA	17.552 μA

Table 3 – *F*-test for DA measurement using SPCE

F-Test Two-Sample for Variances		
	First day	*Second days*
Mean	10.7966	16.3924
Variance	0.1457853	1.0582528
Observations	5	5
Df	4	4
F	0.137760373	
P (*F* < = *f*) one-tail	0.040431139	
F Critical one-tail	0.156537812	

Table 4 – *t*-test for DA measurement using SPCE

t-Test Two-Sample Assuming Equal Variances		
	First day	*Second days*
Mean	10.7966	16.3924
Variance	0.1457853	1.0582528
Observations	5	5
Pooled Variance	0.60201905	
Hypothesized Mean Difference	0	
df	8	
t Stat	11.4032087	
P (*T* < = *t*) one-tail	1.5797E-06	
t Critical one-tail	1.85954804	
P (*T* < = *t*) two-tail	3.1594E-06	
t Critical two-tail	2.30600414	

Dopamine can be detected specifically by looking at its reduction peak signal at a potential of -0.02 V ($i_{pc1} = -38.882$ μA and -0.544 V ($i_{pc2} = -38.791$ μA) without any interference signals from ascorbic acid, glucose, uric acid, paracetamol, and urea Fig. 6.
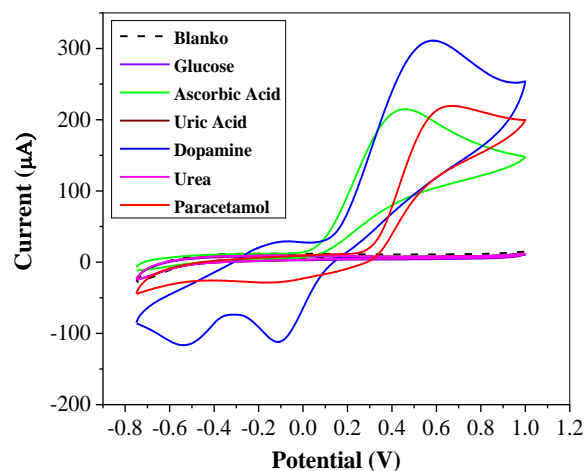

Fig. 6 – Voltammogram of 10 mM dopamine, ascorbic acid, glucose, uric acid, urea, and paracetamol solution in phosphate buffer pH 7.0 using SPCE

4. CONCLUSIONS

The performance of the SPCE demonstrates a selective sensor for DA detection in neutral conditions (0.1 M phosphate buffer, pH = 7.0). The selectivity of SPCE can be shown in the reduction peak of DA without the interference of urea, glucose, ascorbic acid, uric acid and paracetamol. The detection limit and sensitivity of the SPCE for DA detection are 0.030 μM and 8.107 μA mm^{-2} μM^{-1}, respectively. DA molecules can poison the surface of SPCE, as indicated by increasing the anodic peak current during five continuous measurements in different days using the same dopamine solution sample.

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Селективний електрохімічний датчик з використанням вугільного електрода з трафаретним друком (SPCE) для виявлення дофаміну в нейтральному стані

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Селективний електрохімічний датчик для виявлення дофаміну (DA) досліджено за допомогою вугільного електрода з трафаретним друком (SPCE). Ефективність SPCE була охарактеризована за допомогою циклічної вольтамперометрії при pH 7,0 в 0,1 M фосфатному буферному розчині. Вимірювання проводили в діапазоні потенціалів від $-7{,}5$ до 1 В при кімнатній температурі. Спостерігали вплив концентрації DA та швидкості сканування. Результат показав, що DA можна виявити спеціально, дивлячись на його піковий сигнал відновлення при потенціалі $-0{,}11$ В, $i_{pc} = -52.13$ мкА. Сигнал DA контролювали без будь-яких інтерференційних сигналів від аскорбінової кислоти, глюкози, сечової кислоти, парацетамолу та сечовини. Отримана калібрувальна крива, яка представляє різні концентрації DA як функцію пікового струму, відповідала лінійному рівнянню $i_{pa} = 3.484 + 0.413x$ з $R^2 = 0.992$ та $i_{pc} = -2.741 - 0.267x$ з $R^2 = 0.985$. Межі виявлення та чутливості SPCE для детектування DA становили відповідно 0,030 мкМ та 8,107 мкА·мм$^{-2}$·мкМ$^{-1}$. Вплив швидкості сканування продемонстрував поведінку, контрольовану дифузією, з реакції між SPCE та DA. Дослідження відтворюваності SPCE показало збільшення значення пікового струму. Це пов'язано з «отруєнням» DA, що призводить до меншої точності повторних вимірювань.

Ключові слова: Дофамін (DA), SPCE, Вольтамперометрія, Нейтральний стан.