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Voltammetric Method for the Determination of Lactic Acid Using a Carbon Paste Electrode Modified with Cobalt Phthalocyanine

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A non-enzymatic lactic acid sensor was fabricated by a carbon paste electrode (CPE) modified with cobalt phthalocyanine (CoPC). The electrochemical behavior of CoPC modified electrode in lactic acid solutions was characterized by cyclic voltammetry. Results showed that the modified electrode exhibits good catalytic activity for the oxidation of lactic acid at 1.18 V versus saturated Ag/AgCl reference electrode. It had an operational pH range of 3.6-1.6 and showed the linear dynamic range from 11.9 mM to 188 mM of lactic acid at pH 2.0 with good reproducibility. The detection limit was found to be 1.54 mM (3σ). Our study also found that ascorbic acid, malic acid, EDTA, oxalic acid, and citric acids were the interfering species to the electrode while melonic acid, maleic acid, fumeric acid, and stearic acid showed no interference effect on the electrode performance.

Keywords: Modified electrode, Cyclic voltammetry, Lactic acid, Electrocatalytic oxidation, Cobalt phthalocyanine, Carbon paste electrode

1. INTRODUCTION

A highly sensitive, selective, and reliable sensor for the monitoring of lactic acid is useful in clinical diagnostics, biotechnology, sports medicine, and food industry [1-7]. In nature, lactic acid exists as two isomers, L-lactic acid and D-lactic acid. L-lactic acid is produced in humans and mammals while D-lactic acid is produced by microorganisms, algae, and plants. In sports medicine, monitoring the blood L-lactate, conjugate base form of the lactic acid, can determine the anaerobic threshold limit of an athlete. The normal blood L-lactate level ranges from 0.44 to 1.78 mM [8]. In the food industry, D-lactic acid plays an ambiguous role. On one hand, it is considered as one of the key component for the taste, pH control, and emulsifier. Cheese, yogurt, and sauerkraut are examples of

foods with high lactic acid content. On the other hand, a high lactic acid level in food is indicative of food spoilage and bacterial contamination [9]. An early detection method for lactic acid in the food packaging could be used to ensure the quality of food, reducing risk of food poisoning and financial loss due to the recall of the food products.

Various methods have already been reported for the detection and determination of lactic acid including amperometric lactate biosensors [6, 10, 11], HPLC [12, 13], GC [12, 14, 15], electrophoresis [16], and spectrophotometric method [17]. Among these methods, the amperometric biosensor is considered the simplest yet offering relatively fast analysis of chemical species and applicability for portable point-of-care devices [18]. But one disadvantage of a biosensor is the unstable nature of the enzyme. Thus, utilizing non-enzymatic electrocatalyst as the sensing element for amperometric detection of lactic acid is highly desirable.

In this paper, we propose a new approach to use cobalt phthalocyanine (CoPC) as a non-enzymatic catalyst for oxidation of lactic acid. The CoPC modified CPE was characterized by cyclic voltammetry. The experiment variables such as solution pH, scan rate, and presence of the interference species are also investigated.

2. EXPERIMENTAL

2.1. Chemical and Apparatus

All chemicals used were of analytical quality. Cobalt phthalocyanine, phosphoric acid, potassium phosphate monobasic, potassium hydroxide, graphite powder and paraffin oil were from Sigma Aldrich and were used as received. L-lactic acid, approx. 93% (J.T. Baker Chemical) and sodium lactate, approx. 93% (Sigma Aldrich) solutions were prepared by dissolving in a 1.0 M pH 2 potassium phosphate buffer. The 1.0 M pH 2 potassium phosphate buffer solution was prepared by dissolving the potassium phosphate monobasic powder in a de-ionized water and adjusting to pH 2 with concentrated phosphoric acid. The stock solution of lactic acid was standardized by titration before the lactic acid standard solutions were prepared. All solutions were prepared with de-ionized water.

2.2 CoPC Modified Carbon Paste Electrode

Carbon paste electrode was fabricated by mixing graphite (67 wt%) and paraffin oil (33%). The CoPC modified electrode was fabricated by mixing graphite powder (67 wt%), paraffin oil (28%), and CoPC powder (5%) using a pestle and a mortar. The modified and unmodified carbon paste was packed firmly into the end of a 1000-mL pipette tip with an aluminum strip inserted in the inner end of the carbon paste for electrical contact. Each electrode was pretreated with potential scans from 0 V to 1.5 V in 0 M pH 2 phosphate buffer solution before the measurements.

2.3. Electrochemical Measurements

All electrochemical measurements were performed by using WaveNow Potentiostat from Pine Instrument Company. A conventional three-electrode system was used with a carbon paste electrode (unmodified or modified), a saturated Ag/AgCl reference electrode, and a Pt wire as the auxiliary electrode. All cyclic voltammetric measurements except the scan rate study were performed by using the linear potential sweep from 0 V to 1.5 V with a scan rate 100 mV s^{-1}.

3. RESULTS AND DISCUSSION

3.1 Electrochemical behavior of lactic acid on CoPC-CPE

The voltammetric (CV) behavior of the lactic acid was studied on the unmodified and CoPC modified CPE in the 1.0 M pH 2 phosphate buffer by cyclic voltammetry. Figure 1 shows two voltmmograms for 141 mM lactic acid in pH 2 phosphate buffer on the modified and unmodified CPE using a scan rate of 100 mV s^{-1}. In an anodic sweep, the current peak at 1.18 V versus saturated Ag/AgCl reference electrode was observed on the CoPC-CPE corresponding to the oxidation of the lactic acid by the CoPC. No cathodic peak was observed in the cathodic potential sweep, suggesting that the oxidation of lactic acid is irreversible.

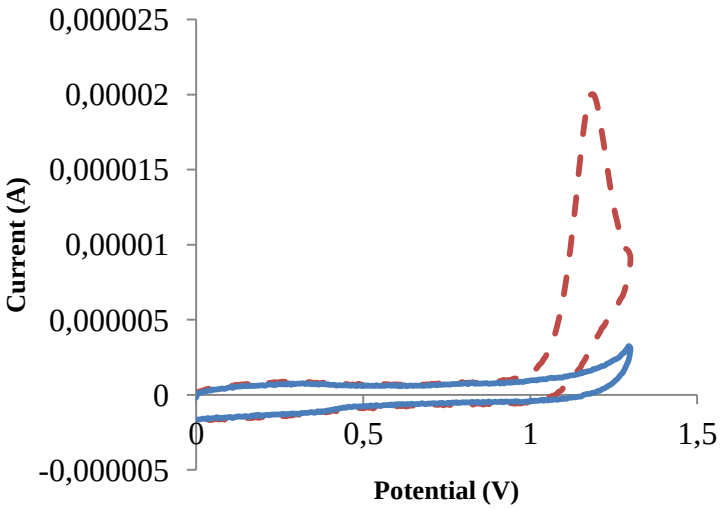

Figure 1. Cyclic valtammograms of 141 mM lactic acid in 1.0 M pH 2 phosphate buffer by unmodified CPE (solid line) and by CoPC-CPE (dash line). The scan rate was 100 mV s^{-1}.

The nature of the lactic acid oxidation was studied by using various potential sweep rates (from 10 to 100 mV s^{-1}). The results showed that the peak current is linearly proportional to the square root of potential sweep rates $v^{1/2}$ (R^2 = 0.9987) shown in Figure 2, indicating that the electrocatalytic oxidation of lactic acid by CoPC is diffusion controlled.

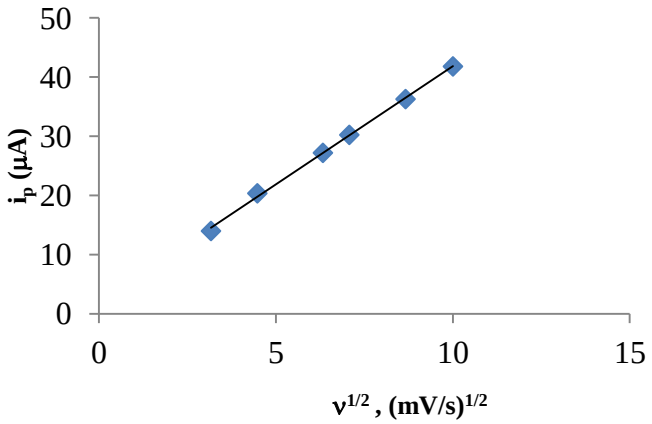

Figure 2. Dependence of the peak current on the square root of the scan rate in 0.141 M lactic acid in 1.0 M pH 2 phosphate buffer by CoPC-CPE. The scan rates are 10 mV s^{-1}, 20 mV s^{-1}, 40 mV s^{-1}, 50 mV s^{-1}, 75 mV s^{-1}, and 100 mV s^{-1}. The concentration of lactic acid is 141 mM in pH 2 phosphate buffer.

3.2 Effect of pH on anodic peak current

The oxidative current of the lactic acid on the CoPC modified CPE are pH dependent as shown in Figure 3. The experiment was performed by adding concentrated phosphoric acid dropwise to 10.0 mL of 141 mM unbuffered lactic acid solution while the anodic peak current and pH were monitored simultaneously. The initial pH was 6.6. The anodic peak of lactic acid on the CoPC modified CPE did not appear until pH decreased to 3.6. As the pH decreases, the peak current increases, an indication of increasing oxidation rate.

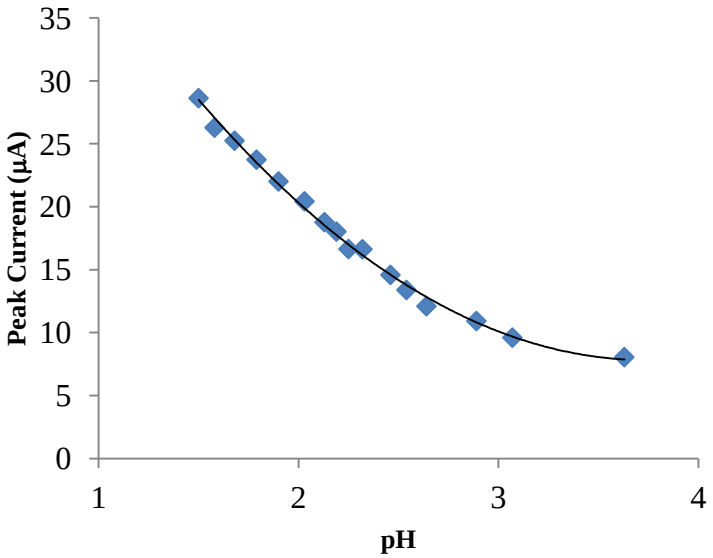

Figure 3. The pH effect on the anodic peak current.

3.3 Determination of lactic acid

The catalytic role of the CoPC-CPE in the electro-oxidation of lactic acid provides a mean for the voltammetric determination of lactic acid. Figure 4 shows an increase in anodic peak current was obtained from increasing lactic acid concentrations in the pH 2 phosphate buffer. The peak

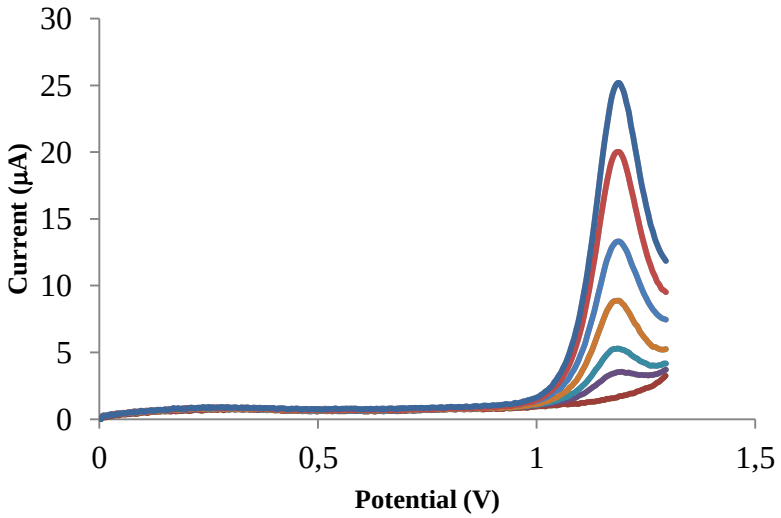

Figure 4. The voltammograms of various lactic acid concentrations in pH 2 buffer. Scan rate: 100 mV s^{-1}. From low to high, the concentrations of lactic acid are 0, 11.9, 23.8, 47.6, 95.2, 141, and 188 mM.

currents shown in Figure 5 for the lactic acid has a linear range from 11.9 mM to 188 mM. The slope and the correlation coefficient (R^2) were 124 µA/M and 0.999, respectively. The detection limit was 1.54 mM when the signal to noise ratio is 3.

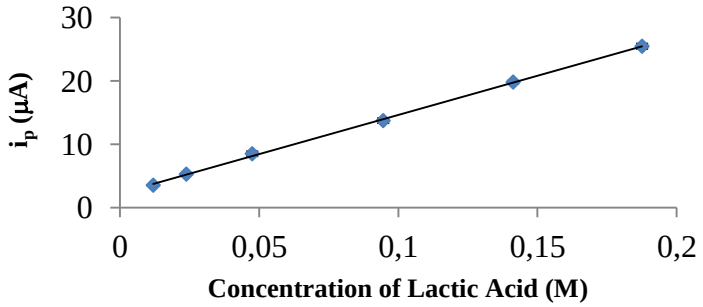

Figure 5. Linear calibration curve of peak current versus of lactic acid concentration. Each point is the average of three readings. Y = 123.6 X + 2.2773 with R^2 = 0.9994

3.4 Interference Study

We examined nine different organic acids: ethylenediaminetetraacetic acid (EDTA), ascorbic, malic, oxalic, citric, malonic, maleic, fumeric, and stearic acid using CoPC-CPE to determine their

possible interference effects on the lactic acid sensing. Figure 6 shows the voltammograms of the interfering organic acids with a concentration of 10.0 mM in pH 2 phosphate buffer.

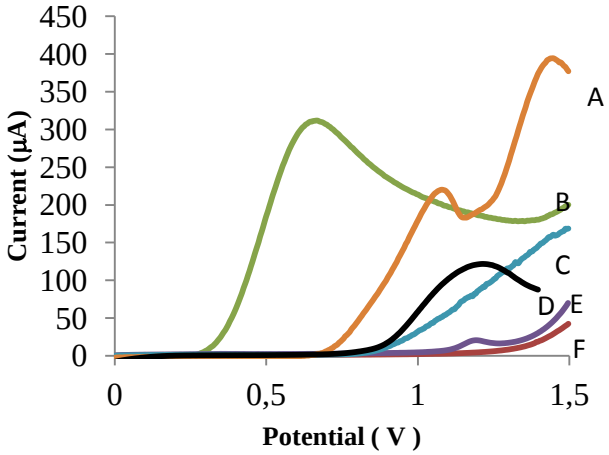

Figure 6. Cyclic voltammograms of the interference organic acids on CoPC-CPE in pH 2 buffer. A. oxalic acid, B. ascorbic acid, C. EDTA, D. citric acid, E. malic acid, F. pH 2 buffer. The concentrations of all organic acid were 10 mM. Scan rate: 100 mV s^{-1}.

At 1.18 V, the voltammograms in Figure 6 reveals that EDTA, ascorbic, malic, oxalic, and citric acids were interfering species to the determination of lactic acid. Other organic acids, malonic, maleic, fumeric, and stearic acids, showed no interference effect towards lactic acid sensing using the CoPC-CPE.

3.5 Repeatability, Reproducibility, and Stability

Measurement of the repeatability and reproducibility of the CoPC-CPE was conducted at a lactic acid concentration of 11.9 mM. The relative standard deviation for a series of ten successive measurements was 0.53% (repeatability) and the relative standard deviation for four individual sensors with the same cross-section areas was 5.6% (reproducibility).

The long term storage stability of the CoPC-CPE was studied by comparing the response of the anodic peak current produced in an 11.9 mM lactic acid solution. The CoPC-CPE was stored in a desiccated container at 20 ^{o}C. The response after being stored over a year showed no significant change.

4. CONCLUSIONS

In this work, an electrochemical sensor based on electrocatalytic oxidation of lactic acid on the surface of CoPC modified CPE was described. Cyclic voltammetry was used and found that the oxidation of lactic acid by CoPC-CPE occurred at 1.18 V versus saturated Ag/AgCl reference electrode in a pH 2 phosphate buffer and that the oxidation process was diffusion controlled. The proposed method has a good linear range from 11.9 mM to 188 mM with a detection limit of 1.54 mM

(3σ). The sensor was susceptible to interference from the presence of EDTA, ascorbic, malic, oxalic, and citric acid at a concentration of 10.0 mM. But ease of preparation, high stability of non-enzymatic CoPC, and its excellent reproducibility of the voltammetric response make it a potential candidate for the quantification of lactic acid in a solution.

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