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Development of C-Pd Electrode as A Working Electrode in The Detection of Dissolved Oxygen by Cyclic Voltammetry

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Abstract: Dissolved oxygen in water is vital in supporting life, so it becomes one of the parameters of water quality and makes dissolved oxygen measurement very important. This study attempts to develop an electrode based on carbon-palladium alloy material (C-Pd) to be used as a voltammetric detector of dissolved oxygen in water. The formation of the alloy is carried out by electrodeposition using the cyclic voltammetry technique. The effect of HCl concentration in the palladium electrodeposition process is studied to obtain the optimum HCl concentration. The resulting C-Pd electrode is then tested for its performance in measuring dissolved oxygen. It is carried out by cyclic voltammetry in NaOH electrolyte solution, Ag/AgCl reference electrode, and Pt counter electrode. Before standard solutions and samples are measured, the NaOH concentration is optimized first to obtain the best oxygen reduction conditions on the Pd surface. The results of oxygen measurements with the C-Pd electrode are compared with those from a commercial DO meter. The results showed that palladium electrodeposition on the carbon surface was optimum in 0.5 M HCl solution, and the optimum dissolved oxygen reduction process used 0.1 M NaOH electrolyte solution. The results of the C-Pd electrode performance test showed a decrease in sensitivity in the form of a calibration curve slope value of -703.77 nA/ppm on the first day, -558.36 nA/ppm on the second day, and -417.81 nA/ppm on the third day. A comparison of measurement results between the C-Pd electrode and a commercial DO sensor showed a significant difference. Despite the less-than-optimal results, this study shows the potential for palladium to be used as an electrode in an electrochemical oxygen sensor as an alternative electrode material besides precious metals.

Keywords: Electrodeposition, Carbon, Dissolved Oxygen, Palladium, Cyclic Voltammetry.

INTRODUCTION

Dissolved oxygen (DO) is one of the important parameters in water quality indicators. Dissolved oxygen is utilized by aquatic organisms to respirate and is required by microorganisms to decompose organic compounds into other simpler and non-toxic compounds. The greater the DO in water, the more it indicates that water has good quality, while if it has a low DO, it means that the water is contaminated [1].

Electrochemical sensors have been developed to measure dissolved oxygen content since they have good sensitivity and are easy to use. One of the electrochemical sensors frequently used to measure dissolved oxygen is *the Clark electrode* [2]. Clark electrode uses platinum (Pt) as a cathode, which is expensive and limited in nature [3]. Thus, it becomes a challenge to find an alternative replacement Pt. Metal palladium (Pd) can replace Pt as the working electrode. Pd has characteristics similar to Pt and is more available in nature [4].

Furthermore, Pd has the same mechanism as Pt in the reduction of O_2 [5]. However, Pd in the form of wire has a small surface area. Electrodeposition is one of the ways to expand the surface area by superimposing Pd on carbon electrodes [6]. As an electrode, carbon has inert quality, a wide potential range, a low background current, and is easy to obtain and affordable. Carbon pores can also trap Pd, making a stronger contact between carbon and Pd.

Research conducted by Mukhakikin [8] shows that N_2O gas sensors using palladium-carbon material have shown a remarkable response, and it is also relatively easy to stick palladium on the carbon electrode surface [7]. C-Pd electrodes are also responsive to O_2 and can be developed as a dissolved oxygen sensor. Asri (2010) [9] states that Pd electrodeposition is less stable in 30 cyclic by using a phosphate buffer solution in a carbon electrode. Pd electrodeposition on the working electrode using acidic media has been widely used to replace the phosphate buffer solution. Chang's research [10] shows that the Pd electrodeposition on carbon electrodes can be done by dissolving K_2PdCl_6 in HCl to get a good performance of Pd electrodeposition.

The voltammetric technique can be implemented in three electrodes separated by an electrolyte solution, where palladium acts as a working electrode. In the voltammetric experiment, Pd(s) was dominantly oxidized back into Pd^{2+} in the acid electrolyte. Therefore, his research uses an alkaline electrolyte as a conductor [11]. In addition, the outside of the sensor is covered by polytetrafluoroethylene membrane (PTFE) as supporting material. These membranes are hydrophobic, inert, relatively strong, temperature-resistant, and permeable to oxygen [12]. This membrane transports dissolved oxygen through diffusion, prevents the leakage of electrolyte solution, and holds back the water. This paper reports the development of a C-Pd electrode for an oxygen sensor; it was characterized based on its working performance, and the results of oxygen measurement are then compared with the results of measurements with the commercial dissolved oxygen sensor.

EXPERIMENTAL

All chemicals used in this research are analytical grade, and solution preparation uses distilled water as the primary solvent. The preparation of C-Pd electrodes and the utilization of C-Pd electrodes were carried out by voltammetry in an electrochemical cell equipped with an Ag/AgCl reference electrode and a Pt counter electrode.

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Electrode polarization was carried out by cyclic voltammetry using a potentiostat (Amel 433A0).

Preparation of carbon rods as electrodes

The carbon rods from type AAA batteries were cleaned and washed using distilled water, and the side surfaces were coated using epoxy resin. The carbon ends were rubbed using alumina powder and then cleaned in an ultrasonic cleaning bath for three minutes. Then, left at room temperature.

Preparation of Pd electrodeposition cell on C

The electrochemical cell consists of three electrodes: a carbon electrode, an Ag/AgCl reference electrode, and a Pt auxiliary electrode, all three of which are immersed in 10 mL of 0.1 M HCl supporting electrolyte solution. This cell is then polarized by cyclic voltammetry at a potential interval of +0.3 V to -0.65 V with a scan rate of 50 mV/s. With the same cell treatment, the Pd electrodeposition process on the surface of C is carried out by replacing the electrolyte solution with a solution containing 0.0198 g of K_2PdCl_6 which is inserted into a 10 mL measuring flask, then 1 mL; 3 mL; 5 mL; 7 mL of 1 M HCl solution is added and added with distilled water to the mark.

Optimization of electrolyte solution concentration in dissolved oxygen measurement

The NaOH electrolyte solution was varied in concentrations of 0.001 M, 0.01 M, and 0.1 M, 0.5 M. The O_2 gas analyte was aerated into 500 mL of distilled water for 30 minutes (saturation concentration around 6.3 ppm), which was then subjected to cyclic potential at -1 to +1 V and a scan rate of 50 mV/s. The optimum NaOH electrolyte solution concentration was obtained from the optimum dissolved oxygen reduction current.

Characterization of C-Pd electrode performance in dissolved oxygen measurement

In this research, the observed sensor performance characteristics were the working area, sensitivity, detection limit, and reproducibility, which can be obtained from measuring the response of the C-Pd electrode to variations in dissolved oxygen concentration. The results of dissolved oxygen measurements in samples using the C-Pd electrode and commercial DO meter were compared using the t-test.

RESULT AND DISCUSSION

Electrodeposition of Pd on the surface of C

The electrodeposition process of Pd on C can be observed from the voltammogram profile when carbon as the working electrode is immersed in a solution of HCl with a particular concentration and then given a polarization voltage from a potentiostat in conditions without K_2PdCl_6 and with the addition of K_2PdCl_6.

Figure 1a shows no oxidation-reduction peak in the voltammogram because no palladium is available in the solution, so electrodeposition does not occur on the carbon surface. Figure 1b shows a difference from that observed in Figure 1a; namely, in the negative scan, there is a reduction peak at a potential of -137 mV, which indicates that there is Pd electrodeposited on the surface of the carbon electrode. A reduction peak is also seen in the area of -337 mV to -357 mV, which indicates that palladium adsorbs hydrogen ions to form PdH.

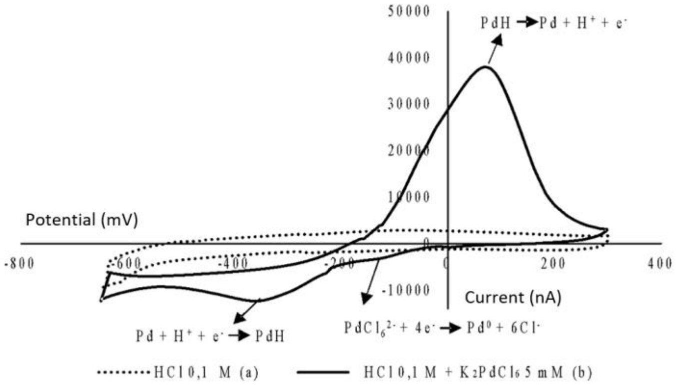

Figure 1. Voltammogram carbon electrode in HCl 0.1 M (a) and HCl 0.1 M + K_2PdCl_6 (b), scanrate 50 mV/s

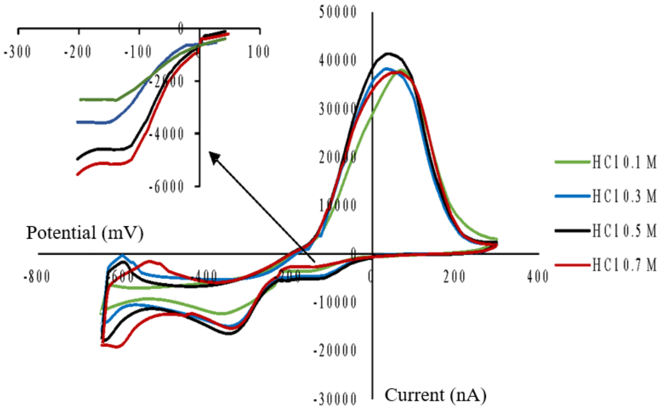

Figure 2. Voltammogram electrodeposition K_2PdCl_6 on carbon with variation HCl solution and scanrate 50 mV/s

Figure 2 shows that in the negative scan, there is a peak of palladium ion reduction current on the carbon working electrode, which occurs at a potential of -135 mV to -154 mV. The reduction current increased up to 0.5 M HCl concentration and decreased at 0.7 M HCl concentration. The decrease in peak reduction current is likely due to the higher H+ concentration, the closer the distance between particles so that the diffusion movement of palladium ions towards the carbon electrode surface was disrupted. These results show that 0.5 M HCl concentration is the optimum concentration for the palladium electrodeposition process on carbon with a current of -4007.61 nA.

Design of Voltammetric Dissolved Oxygen Sensor

Carbon-palladium electrodes (C-Pd), Pt counter electrode, and reference electrode Ag/AgCl are put in a tube made of PTFE, where the dissolved oxygen electrodeposition process occurs. An optimum electrolyte solution of NaOH separates those three electrodes, while one end of the tube is closed with a permeable polytetrafluoroethylene (PTFE) membrane.

Figure 3. Design of dissolved oxygen carbon-palladium (C-Pd) sensor

PTFE membranes are stable, inert, and permeable to water, so dissolved oxygen can pass through diffusion. They are hydrophobic to prevent the leakage of electrolyte solution and to hold water from entering the PTFE tube. The electrolyte solution of NaOH serves as a conduction medium of dissolved oxygen to approach the working electrode surface for reduction. Application of cyclic potential -1000 mV s/d 1000 mV and scanrate 50 mV/s by the potentiostat will cause an oxidation-reduction reaction that produces measured current displayed as a voltammogram.

Optimization of Electrolyte Solution

Optimization of NaOH electrolyte solution begins with creating a profile of carbon-palladium electrode voltammogram (C-Pd) in an electrolyte solution of 0.1 M NaOH in zero oxygen concentration and oxygen saturated solution to determine peak oxidation-reduction of dissolved oxygen. Figure 4 shows that there are no reduction and oxidation peaks in zero concentration of oxygen. Meanwhile, the condition of the oxygen saturation (6.00 ppm) has a different case. In the negative scan, the PdO reduction peak is visible around the -310 mV potential region with a current of -4551 nA, and it shows the adsorption peak PDH hydrogen formed in the potential region -727 mV with a current of 4900 nA. In the positive scan, the visible peak in the potential region -932 mV indicates PdH desorbing. Furthermore, the oxidation peak at -787 mV region marks the formation of PdOH, and the small peak at 12 mV marks the formation of PdO.

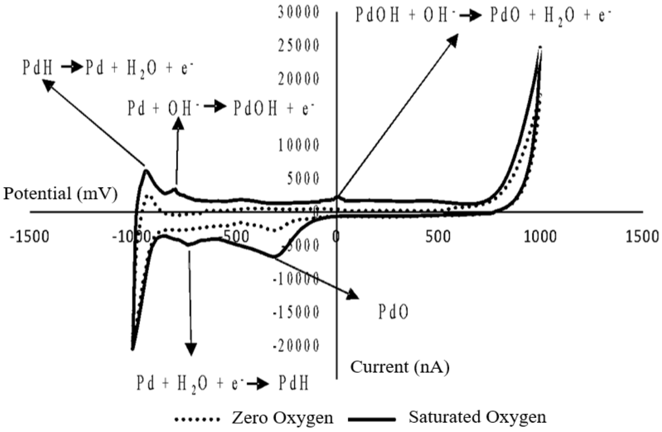

Figure 4. Voltammogram dissolved oxygen reduction using C-Pd electrode in NaOH 0.1 M and scanrate 50 mV/s

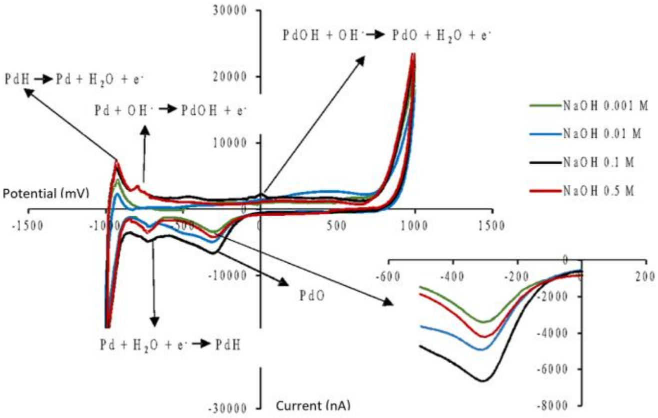

Figure 5. Voltammogram dissolved oxygen reduction using C-Pd electrode in variation NaOH concentration and scanrate 50 mV/s

Based on Figure 5, different concentrations of NaOH electrolyte solution produce different reduction peaks. The optimum concentration of NaOH electrolyte is 0.1 M, in which the reduction process of oxygen occurs at a potential of -309 mV with a current reduction of -4551.11 nA. A concentration of 0.1 M is ideal for the dissolved oxygen reduction process. The more ions Na+ and OH- blocking dissolved oxygen into carbon-palladium electrode surface (C-Pd) to experience reduction causes a decrease in current reduction peak at a concentration of 0.5 M NaOH.

Characterization of C-Pd Dissolved Oxygen Sensor

The performance characterization of the C-Pd dissolved oxygen sensor was carried out for three consecutive days using the same treatment each day to assess the parameters of the linear region, sensitivity, detection limit, and reproducibility. In addition, a comparative test of the measurement results of water samples with a commercial DO meter was also carried out.

Linear Region

The linear region of the calibration curve is taken from an area that has good sensitivity and regression, namely with an R-value above 0.9. From the measurement of the standard solution for three days, as shown in Figures 6, 7, and 8, it can be stated that the oxygen sensor based on the C-Pd electrode works well in the oxygen concentration range of 1.3 ppm and 6.0 ppm.

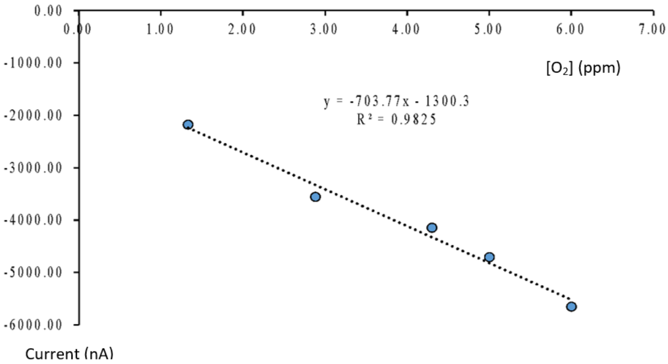

Figure 6. Calibration curve dissolved oxygen using dissolved oxygen C-Pd sensor in first day

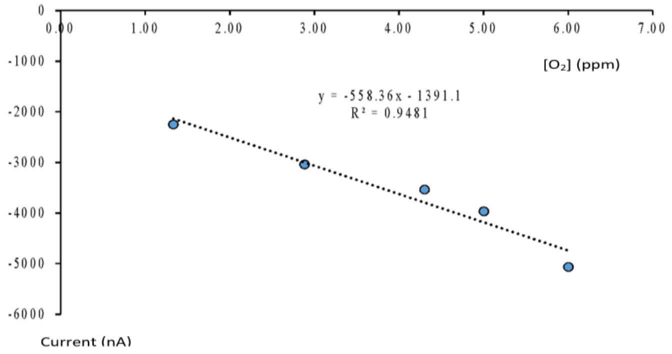

Figure 7. Calibration curve dissolved oxygen using dissolved oxygen C-Pd sensor in second day

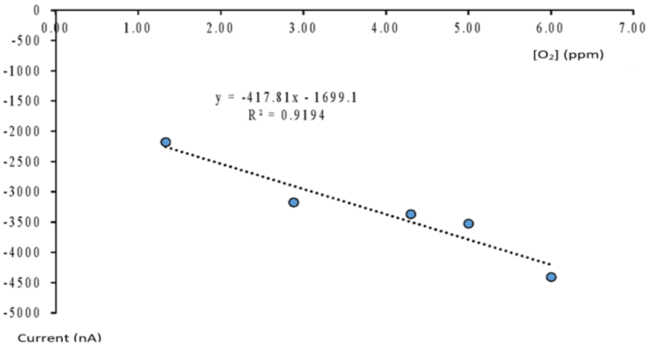

Figure 8. Calibration curve dissolved oxygen using dissolved oxygen C-Pd sensor in third day

Sensitivity

The sensitivity value of the C-Pd dissolved oxygen sensor is expressed by the slope of the linear regression equation of the calibration curve in measuring variations in dissolved oxygen concentration of 1.33 ppm, 2.88 ppm, 4.30 ppm, 5.00 ppm, and 6.00 ppm. Based on Figures 6, 7, and 8, the sensitivity values of dissolved oxygen on the first, second, and third days are -703.77, -558.36, and -417.81, respectively. These sensitivity values explain that each change in ppm concentration of dissolved oxygen results in a change in reduction current of -703.77 nA, -558.36 nA, and -417.81 nA, respectively. The negative sign indicates that the measured current is a reduction current. From these measurement data, it can also be seen that there is a decrease in sensitivity where the measurement on the first day is more sensitive than the second and third days.

Detection Limit

The detection limit is the amount of analyte concentration in the sample that can still be detected and provides a significant response compared to the blank. The smaller the concentration of dissolved oxygen detected by the C-Pd dissolved oxygen sensor, the better the sensor's performance. Based on the calibration curve equation, the detection limit calculation is obtained at 0.85 ppm, which means that below this concentration, the C-Pd working electrode cannot detect the presence of dissolved oxygen properly.

Reproducibility

Reproducibility is the repeatability or precision of a C-Pd dissolved oxygen sensor measurement result. Reproducibility is obtained from the coefficient of variation, where the lower the coefficient of variation value, the better the reproducibility of the C-Pd dissolved oxygen sensor. Based on Figure 9, it can be seen that the lowest coefficient of variation value is 1.28%, and the highest is 8.49%. The increasing coefficient of variation value indicates a decrease in the response of the C-Pd sensor to dissolved oxygen, possibly due to impurities covering the palladium surface on the carbon. The impurity layer is possible to be Pd-H.

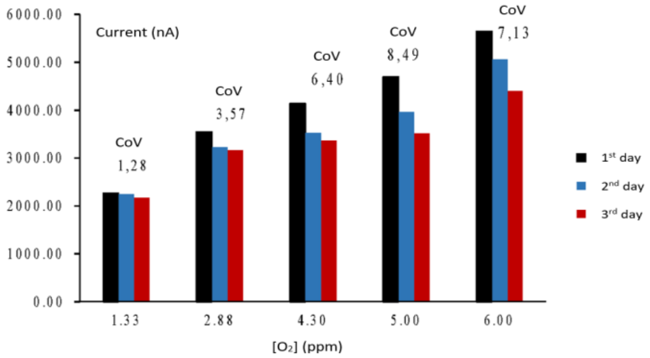

Figure 9. Reproducibility of dissolved oxygen C-Pd sensor

Comparison of measurements

The t-test evaluates the measurement results between the C-Pd dissolved oxygen sensor and the commercial dissolved oxygen sensor (DO meter). Table 1 shows that the dissolved oxygen concentration value measured by the DO meter is always greater when compared to the C-Pd dissolved oxygen sensor. It is unknown whether this difference indicates that the DO meter is more sensitive to dissolved oxygen than the C-Pd dissolved oxygen sensor or whether there are other influences. Based on the results of the t-test, it can be seen that with a 95% confidence level, the t-value for the difference in dissolved oxygen measurements does not fall within the range of $-2.13 \leq$ t-count ≤ 2.13, meaning that statistically, there is a significant difference.

Table 1. Measurement of dissolved oxygen samples using C-Pd sensor and DO meter

Sample	DO Meter	C-Pd Dissolved Oxygen Sensor
Tap water	4,1 ppm	3,6 ppm
Well water	3,8 ppm	2,2 ppm
Pool water	5,3 ppm	4,6 ppm

CONCLUSION

The optimum concentration of the HCl solution in the palladium electrodeposition process on carbon is 0.5 M with a potential of -137 mV and a current value of -4007.61 nA. Meanwhile, the optimum concentration of the NaOH electrolyte solution in the dissolved oxygen reduction process is 0.1 M with a potential of -310 mV and a current value of -4551.11 nA. The measurement performance of the C-Pd dissolved oxygen sensor still needs to be improved, especially in sensitivity and lifetime, because there was a significant difference in measurement results with commercial DO meter measurements and a decrease in sensitivity within three days.

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