

Iridium Oxide pH Sensor Based on Stainless Steel Wire for pH Mapping on Metal Surface

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ABSTRACT

A simple technique to fabricate the iridium oxide pH sensor is useful in several applications such as medical, food processing and engineering material where it is able to detect the changes of pH. Generally, the fabrication technique can be classified into three types: electro-deposition iridium oxide film (EIROF), activated iridium oxide film (AIROF) and sputtering iridium oxide film (SIROF). This study focuses on fabricating electrode, calibration and test. Electro-deposition iridium oxide film is a simple and effective method of fabricating this kind of sensor via cyclic voltammetry process. The iridium oxide thick film was successfully electrodeposited on the surface of stainless steel wire with 500 cycles of sweep potential. A further analysis under FESEM shows detailed image of iridium oxide film which has cauliflower-like microstructure. EDX analysis shows the highest element present are iridium and oxygen which concluded that the process is successful. The iridium oxide based pH sensor has shown a good performance in comparison to conventional glass pH sensor when it is being calibrated in buffer solutions with 2, 4, 7 and 9 pH values. The iridium oxide pH sensor is specifically designed to measure the pH on the surface of metal plate.

Keywords: pH sensor; iridium oxide; electro-deposition; cyclic voltammetry; thick film, coating

1. INTRODUCTION

pH sensors have been applied in a multi-discipline industries such as chemical, biomedical, electro-biomedical and materials engineering where pH is involved in many control processes [1]. The conventional pH sensors which are basically made up of glass electrode have been widely used in pH measurement applications [2, 3]. In general, the conventional glass-type electrode has several good characteristics like good sensitivity, stability and long lasting. In addition to those advantages, glass-type has property of relatively low electrical resistance and shows no sensitivity to any kinds of redox species, gasses, anions or busser [4]. However, this electrode still has drawbacks in term of fragility and it is not suitable to be used in certain applications in biomedical, clinical and food industries [3]. In biomedical and physiological fields for example, glass electrodes have difficulty of miniaturization, poor response time and defenseless to membrane fouling [4]. In term of preservation, it is hard to maintain the quality and it always failed in harsh environmental condition [5]. Glass type electrodes for pH sensor are high cost, hard to fabricate and sensitive to certain alkaline and fluorhydric acid solution [1]. The fabrication technique for producing iridium oxide pH electrode sensor varies and it depends on the applications of sensor. Several popular fabrication processes which have been used to produce this type of sensor including sputtering [2-6], thermal oxidation [2-4,6] thermal decomposition [5,6], electrochemical growth [2,3,6], sol-gel [3,4] and electro-deposition [2,4,6]. Sputtering iridium oxide film (SIROF) method is excellent in terms of high production output and it is able to fabricate up to sub-micron-size. Sputtering requires expensive materials and instrumentation [2].

SIROF is an efficient way for producing high quality of iridium oxide film and at a high cost [3, 7]. Anodic iridium oxide thin film (AIROF) is an economic approach for producing iridium oxide film. AIROF is just an electrolysis process that basically uses a solution of iridium complexes. Iridium tetrachloride compound is an example of deposition



agent [3]. The deposition of efficiency depends on pH value of deposition solution, temperature of solution and current density [3].

On contrary to conventional glass pH electrode, metal/metal-based pH sensor has a quicker pH response. Several solid-state metal oxides which are suitable for pH sensors include PtO_2 , IrO_x , RuO_2 , OsO_2 , Ta_2O_5 , RhO_2 , TiO_2 , PaO_2 , $\text{Sb/Sb}_2\text{O}_3$, WO_3 , PbO_2 , Co_3O_4 and SnO_2 [2-5,8]. The most suitable metal oxide of all is IrO_x and shows great stability in any pH condition. Moreover, IrO_x is still able to work in a high surrounded temperature up until 250°C [1-3], pressure up to 270 bars [2, 9]. In addition, IrO_x has a quick response time, minimum chemical interference as well long-term stability [2-4], good response to the hydrogen ion [5] and low in term of impedance, toxicity and reactivity [10].

There are three possible mechanisms that might be involved in pH dependent redox reaction [2, 3] as follows:



The redox potential is defined as follows:

$$E = E^\circ - 2.303 (RT/nF) \text{pH} = E^\circ - 0.059\text{pH} \quad (4)$$

The value of E° is 926mV which is the standard electrode potential for a standard hydrogen electrode (SHE). F is for Faraday's constant with a value of 96487Cmol^{-1} , n is the number of electrons transfer during redox process. To simplify, RT/F can be replaced with 25.69mV at temperature 25°C . The pH potential sensitivity yields -59mV/pH and this is called as Nernstian response [2, 3].

Iridium oxide film electrode are used as micro-stimulation electrode [11, 12] because Q_{inj} value can be about 4mC/cm^2 [13-15]. On the other hand, iridium oxide film electrodes can exhibit a more charge storage capacity that it is related to reversible Faradaic reactions which causes good biocompatibility and corrosion resistance. This reaction is between Ir^{3+} and Ir^{4+} redox states [16, 17].

This paper focuses on investigation of pH upon a metal surface that is immersed in a solution. Therefore, one probe must be electrodeposited and one device must be designed and implemented for pH monitoring upon immersed-metal surface in solution.

2. EXPERIMENTAL

A. Solution Preparation

The electro-deposition solution was prepared. 150mg of Iridium (IV) chloride hydrate was added in 100mL of distilled water into a 200mL glass beaker. The mixture of solution was stirred by a magnetic stirrer for 10 minutes to dissolve completely. Next, 360mg of oxalic acid was added to the solution followed by stirring about 10 minutes. Then, 1mL of aqueous 30% hydrogen peroxide was added to the solution and stirred for 15 minutes. Lastly, the pH of solution was first recorded about 5 and it shows that the property of solution is quite acidic. Anhydrous potassium carbonate was gradually added to the solution and stirred for 15 minutes until pH reaches 10.5. At the end of the procedure, the color of solution completely turned to light yellow. The solution was transferred into a bottle and allowed to stabilize for two days in room temperature and its color would gradually change to dark blue.

B. Working Electrode Base Fabrication

The working electrodes for deposition process were fabricated and basically made of stainless-steel wire. Two types of wire diameters were used for making working electrodes (pH sensor probe) with 0.25mm and 0.6mm. These 304-

stainless steel wire were mounted in a mixture of epoxy and hardener. Ratio of 2g hardener and 10g of epoxy were used and followed by stirring the mixture for about 5 minutes. A rotating grinder machine with different size of sandpapers grit were used to grind the working electrodes. The grinding process was done using sandpaper with a grade from 180 to 1500 grit at a speed of 120rpm.

C. Electro-deposition method

This is an important process where the growth of iridium oxide layer took place via cyclic voltammetry method. The cyclic voltammetry method basically consists of several electrodes which are being connected to a potentiostat [18]. The Metrohm PGSTAT 128N potentiostat by Autolab was used in electro-deposition coating of iridium oxide via cyclic voltammetry. Three electrodes were used which primarily consist of Ag/AgCl reference electrode, mesh Pt counter electrode and working electrode. These electrodes were connected to potentiostat with wires which have its own color code, blue (reference electrode), black (counter electrode) and red (working electrode).

The process was started by preparing the lab-made electro-deposition bath which used 100ml beaker to hold the solution. The solution was poured until it reached a point where the tip of all electrodes is fully immersed. To ensure the electro-deposition process could occur, the tip of working electrode which has a polished circular cross section area stainless steel wire should be fully immersed. The growth of iridium oxide layer took place only on the exposed area of stainless steel. Figure 1 shows the electrodes setup for electro-deposition process by cyclic voltammetry method.

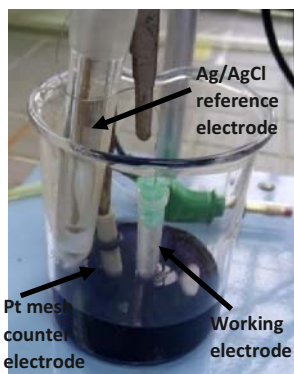


FIGURE 1: Electrodes setup

D. pH Sensor Calibration

The fabricated iridium oxide pH sensors are measured under the open circuit potential to measure the potentiometric response toward several buffer solutions. This process is conducted to study the dynamic range of pH sensor under several buffer solutions. At the end of the process, the calibration curve of pH sensor was obtained. Buffer solutions used are with 2, 4, 7 and 9 pH values. Open circuit potential of iridium oxide pH sensor was measured as a function of pH of buffer solutions respected to Ag/AgCl reference electrode.

E. Prototype Fabrication

The iridium oxide pH micro-sensor was calibrated and tested by mapping the pH value at the surface of a sample. The process is basically the similar to SECM where the probe or sensor is needed to be moved steadily in X and Y axes [19]. Z axis basically controls the distance of the tip of pH sensor to the surface of sample. For this project, X and Y are the main axes that control the movement of the pH sensor in X and Y directions. The position of Z direction was controlled manually using a screw mechanism. This prototype was fully controlled by a microcontroller which mainly works based on C++ program. Before writing program codes, several parameters such as the length and the width of

sample were determined. The scanning process should be within the range of parameters. Figure 2 shows the X-Y plotter prototype [19].

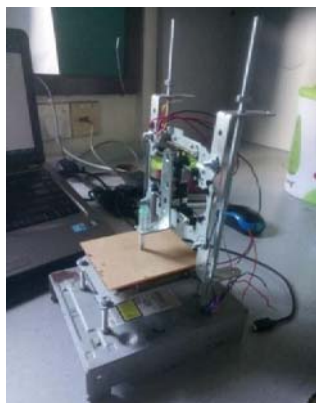


FIGURE 2: X-Y Plotter

The X-Y plotter was controlled by a computer through C++ language program. Therefore, an open-source electronics platform based on hardware and software is required to perform such task. The Arduino electrical board was used as a main processor to translate the input program becoming output which basically the motion in X-Y direction. Of all Arduino products, the Arduino Uno was selected as a microcontroller board for this project. In addition, it has 14 digital input/output pins, 6 analog inputs, USB connection and power jack making it as a suitable platform for this study.

Motor driver is a little current amplifier that primarily takes a low current control signal from microcontroller and turns it into a higher current signal that can drive a motor. Two units of L293D motor driver integrated circuit which has 16 pins were used to control two stepper motors. L293D works based on the concept of H-bridge which is a type of circuit that allows the voltage to flow in two directions. DC motors that can move in discrete steps are called as stepper motors. Stepper motors have multiple coils that are assembled in groups called as “phases”. Energizing each phase with a correct sequence, the motor will rotate with a desired rotation. A very precise positioning and speed can be obtained by using a computer controlled stepping such as Arduino Uno. In this study, a screw-type stepper motor was used to generate linear displacement motion in X and Y.

F. pH Mapping

The iridium oxide pH sensor was used along with the X-Y plotter to measure the pH on the surface of metal. The process was conducted in such a way that its probe tip is partially immersed in electrolyte solution. The sample for test must be fully immersed on the 0.1M sodium chloride solution. During the process, tip of pH sensor was not directly contacted to the surface of sample and held with the same or constant distance. Four electrodes systems were used which consist of working electrode (pH sensor), platinum as a counter electrode, Ag/AgCl as a reference electrode and the sample itself as a substrate electrode. Surface generation tip collection mode (SG/TC) was used to measure the voltage and current generated by the surface of sample. Figure 3 shows the electrodes setup for pH scanning experiment.

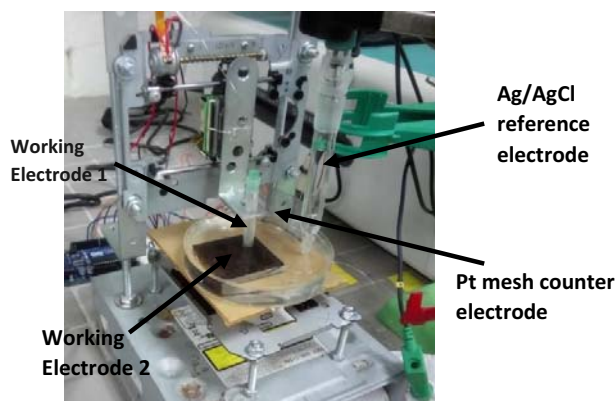


FIGURE 3: pH scanning electrodes setup

3. RESULTS AND DISCUSSION

A. Electro-deposition

The electro-deposition process was conducted by using a cyclic voltammetry method to develop iridium oxide layer on the circular cross section area of stainless steel at the tip of working electrode. Two types of stainless steel wire with diameters of 0.25mm and 0.6mm were electrodeposited separately via cyclic voltammetry method. All parameters for these electro-deposition processes were kept constant at all time. Based on the obtained data, the electro-deposition process was conducted which roughly took 14006 seconds (3 hours and 53 minutes) to complete. In the end of the process, a layer of dark blue, as shown in Figure 4, indicates that the electro-deposition of iridium oxide via cyclic voltammetry was found.

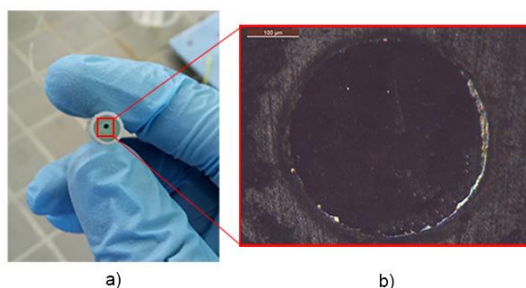


FIGURE 4: (a) Electrodeposited iridium oxide film. (b) Iridium oxide film under optical microscope at 100µm scale.

The cyclic voltammetry process was applied to the working electrodes and the result is shown in the graph. The progress and the pattern of graphs were observed in every 100 cycles. Graphs with potential respective to reference electrode against current were plotted to observe its correlation. In cyclic voltammetry, there are two points that give information about the redox activity during the process and located at the highest and lowest peak of cyclic voltammogram. Based on Figure 5, the cathodic potential peak was recorded at 0.57v with cathodic current peak of 0.141mA. On the other hand, the anodic peak potential was recorded at 0.19V with anodic current peak of -0.502mA.

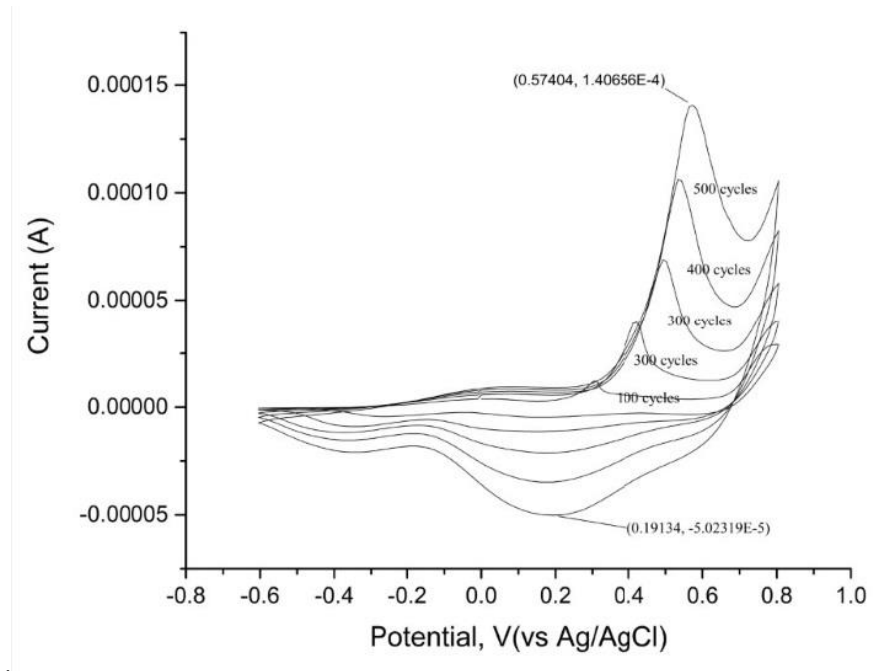


FIGURE 5: Cyclic voltammetry graph of electro-deposition iridium oxide film

B. FESEM Analysis

The microstructure was conducted by using SUPRA 55VP Field Emission Scanning Electron Microscopy (FESEM). FESEM gives a clear topographical and elemental information about the surface with unlimited depth of field. The first microstructure image was taken with 1000X magnification and it shows unevenly distributed growth of iridium oxide film. At certain area, the iridium oxide growth was in a huge lump size while the rest is just average in size, as shown in Figure 6.

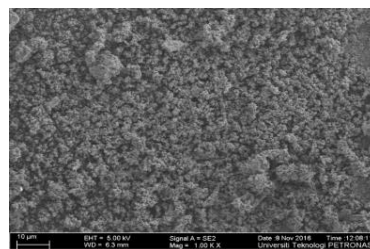
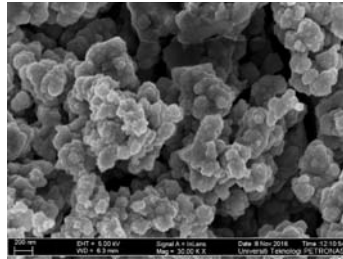


FIGURE 6: FESEM image at 1000X magnification

In order to get a more detailed observation, the magnification was increased to 30000X and it has been focused at area that has a rougher iridium oxide surface. Iridium oxide has cauliflower-like appearance and usually occurred in thicker films. Laterally, high roughness of iridium oxide film gives higher surface area and results in high surface exposure to test environment and better response to pH changes [20]. Figure 7 shows the FESEM image of coating at 30000X magnification. The growth of iridium oxide film is perpendicular to the surface of coated-stainless steel wire.

FIGURE 7: FESEM image of IrO_x at 30000X magnification

C. EDX Analysis

EDX analysis was conducted after observation of microstructure to determine the elemental information about iridium oxide film. From the result of EDX analysis in Figure 8, it shows that the highest element recorded is iridium followed by oxygen. These two elements indicate that the EIROF process is successful. Other types of element such as chromium and iron are also found, they are the main composition of stainless steel.

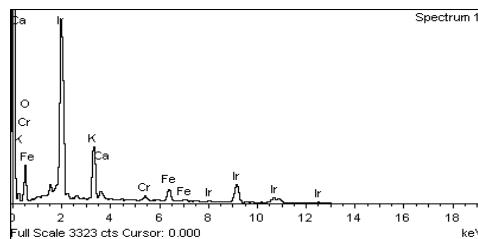


FIGURE 8: EDX analysis result

All elements present on coated-stainless steel wire were analyzed and calculated in term of weight and atomic percentage (Table 1). As shown in Table 1, weight and atomic percentage of oxygen and iridium are significant compared to other materials. This shows that stainless steel wire is coated with IrO_x truly.

TABLE 1: Composition weight and atomic percentage of material for coated- stainless steel wire

Element	Weight	Atomic %
O	23.4	66.79
K	11.14	13
Ca	0.71	0.81
Cr	1.49	1.31
Fe	5.27	4.31
Ir	57.99	13.78
Total	100	

D. Potentiometric Response

The potentiometric response of iridium oxide pH sensor was measured during the open circuit potential experiment by immersing it into buffer solutions with pH of 2,4,7,9. The iridium oxide pH sensor was dipped and left until the reading of average voltage is stable. Figure 9 shows potential, $E(\text{Ag}/\text{AgCl})$ versus pH is plotted to obtain the calibration curve. The iridium oxide pH sensor shows a good linear relation, $R=0.9986$ with super-Nerstian response value of $-0.0779\text{V}/\text{pH}$.

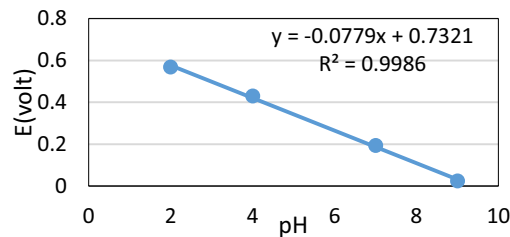


FIGURE 9: Calibration curve of iridium oxide pH sensor E versus pH

E. pH Mapping

The metal plate with 4cm × 4cm dimensions was used for sample as shown in Figure 10. A visual observation after test was conducted and it was found that there are some corrosions on its surface. The sample was further examined to get reading of pH by pH sensor scanning probe. Probe scans the whole surface of substrate step-by-step and collect pH of the surface.



FIGURE 10: 4cm X 4cm metal sample plate

At the end of mapping process, a topographical image of metal surface was obtained showing the distribution of pH as shown in Figures 11-a and 11-b. The Figure shows that the lower region of metal plate has low pH reading which is indicated in red and yellow color. Blue and dark blue of surfaces on the other hand, are due to high pH area of substrate. Therefore, these areas with high pH value are disposed to corrosion. Hence, to prevent of corrosion, these areas must be protected through coating, cathodic protection or other methods. In general, with this method, it can detect pH value upon surfaces that it determines properties and activities of surfaces. As shown in Figure 10, corrosion occurred after test, as pH mapping was predicted. For more detailed analysis, 3D pH contour graph was plotted as shown in Figure 11-b, it is showing that the lowest pH region is on the red part of metal plate.

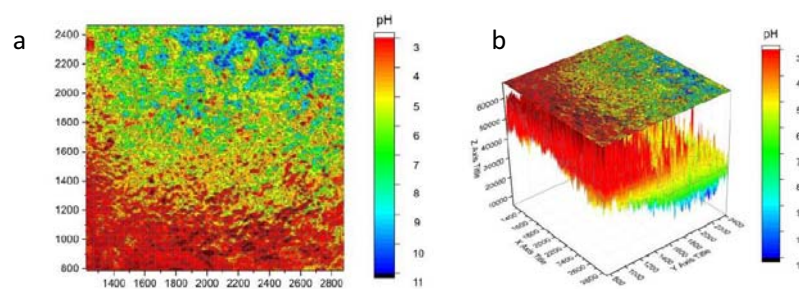


FIGURE 11: a) Topographical and b) 3D topographical images of pH

4. CONCLUSION

The pH microsensor made of stainless steel with coated-iridium oxide film has been successfully developed. Electro-deposition of iridium oxide film (EIROF) is a good and cost-effective technique to produce iridium oxide pH sensor compared to other techniques. Stainless steel is an alternative material to use as substrate for coating. This pH sensor has a good linear response within pH range of 2 to 9 with sensitivity -0.0779V/pH. For the application, the pH sensor

was used to record the reading of pH at the metal surface which give a topographical image based on pH scale. It can determine activities of surface in solution, quality of coatings, properties of surface in different solutions, investigation of biomedical and biological knowledge.

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