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Novel pH sensor based on fiber optic coated bromophenol blue and cresol red

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Abstract

Fabrication of pH sensor based on fiber optic coated bromophenol blue and cresol red has been done. Briefly, jacket in the middle part of the fiber optic was removed for 5 cm. Then the core of each of fiber optics was washed in ethanol. Nitric acid, demineralized water, and ethanol again consecutively. Then the cleaned core was coated using active material using sol-gel immobilization technique. Tetraehyl orthosilicate was used as a binder in the immobilization of active materials. Bromophenol blue will start change the color to yellow at below pH 3.00±0.01 and blue at above pH 4.60±0.01, while the cresol red will start change the color to yellow at below pH 7.20±0.01 and violet at above pH 8.80±0.01. The pH sensors which have been made show the sigmoidal response over pH from 1.00±0.01 to 11.00±0.01. The sensor has a better performance in comparation with the other sensor.

Keywords*: bromophenol blue, cresol red, fiber optic, pH sensor*

1. Introduction

The power of Hydrogen (pH) plays important role in industry and research [1–15]. The simplest way to measure pH of solution use litmus paper, but it can only distinguish either base or acid condition without knowing the exact pH value. The other paper which can be used for measuring pH value is universal indicator paper which have better sensitivity to distinguish the pH value until 0.5 pH scale. The next generation in pH measurement is pH electrode after the invention of glass membrane which sensitive to pH. It is known with the pH meter after equipped with a special electronic system which its sensitivity could reach 0.01 pH scale. The principle of this pH meter is based on Nernst's law which involve the equilibrium of H^+ concentration from inner solution and H^+ from outer solution, and in turn it generates a certain potential between the anode and the cathode. Measurement range of pH electrode is decent that is from 0.0 to 14.0. The weakness of this type pH device has rigid shape, relatively big (it requires reference electrodes) and fragile (the glass membrane part) [1, 5, 16, 17].

In the recent days, various attempts have been made to developed instrument to measure the pH of solution. One of them, which is being developed, is pH sensor based on fiber optic. Fiber optic has been widely studied for many applications including as sensors [18–26]. Fiber optic as pH sensor has several advantages such as flexible, immune to electromagnetic interference, allow the sensor to be used on limited space or hazardous environment, and ability to be miniaturized [26–31]. This kind of pH measurement method is still developed since the research started [32–34]. The popular one is pH sensor based on fiber optic that is coated with active materials which sensitive to H^+ activity in solution, such as pH indicator/dye pH sensitive, using sol-gel technique. The active material is used to replace the cladding layer on the fiber optic. The sol-gel technique can immobilize active materials on fiber optic when the porous matrix layer formed. Then this layer will trap the active materials [35].

The sensor of pH based on fiber optic by sol-gel immobilization method that uses only one pH indicator has been widely studied. In this paper, we report the fabrication of pH sensor based on fiber optic coated with two pH indicator simultaneously using sol-gel immobilization

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technique. The result shows that the pH sensor based on fiber optic can work well over pH 4.50±0.01 to pH 11.00±0.01.

2. Research Method

2.1. Chemicals and Materials

Tetraehyl orthosilicate (TEOS), acetic acid, bromophenol blue, and cresol red were purchased from Merck. Sodium hydroxide and demineralized water were purchased from PT. Brataco. Nitric acid was purchased from SAP Chemical. Three pieces of fiber optic (FD-620-10) cables were bought from Autonics Korea, and were used in all experiment. Ethanol 95% was purchased from OneMed and purified using rotavapor from Buchi prior to be used, while other chemicals were used without any further purification.

2.2. Preparation of Fiber Optic

Three pieces of fiber optics cables were prepared and marked as A, B, and C. Each fiber optic was cut to 45 cm in length. The jacket of each fiber optics was removed for 5 cm length about at the middle part (20-25 cm from the end of the fiber optic cable) of the fiber optic cable. Afterward, the cladding of the fiber optics was abraded using emery paper of grade 1000. Then core of the fiber optic that has been cleaned from the jacket and the cladding, was immersed in ethanol (which was prepared at section 2.1). Furthermore, the core was immersed in a nitric acid 30% for 5 minutes, followed by immersion in demineralized water, and washed using ethanol. This was a designated area of the fiber optic which ready to be coated using pH-sensitive gel as explained in the section 2.3.

2.3. Preparation of Sol-gel Cladding

The pH-sensitive gel was prepared by mixing 41 mg of bromophenol blue, 23 mg of cresol red, 15 ml of TEOS, 15 ml of ethanol, and 1 ml of demineralized water. The mixture was heated at 60°C under stirring condition for 60 minutes. This mixture was used for pH sensitive gel in the following step: The fiber optic which has been prepared in the section 2.2 was ready to be coated using the mixture of pH sensitive gel at a designated area. This designated area of fiber optic was dipped in a pH-sensitive gel for 5 minutes. This step was repeated for two others fiber optic which were prepared in the section 2.2. The pH-sensitive gel modified fiber optic was dried at ambient temperature and atmospheric pressure for 20 days. These pH-sensitive gel modified fiber optics were ready to use for pH measurement.

2.4. Instrumental Setup

Three pH sensors prepared in the section 2.3 were characterized. The instrumental setup can be seen at Figure 1. To obtain the correlation between pH and potential, pH sensor dipped into the solution of various pH. Any change to the pH will automatically recorded which potential is transmitted by the use of digital multimeter photodiode associated with the use of software keithley multimeter 2100.

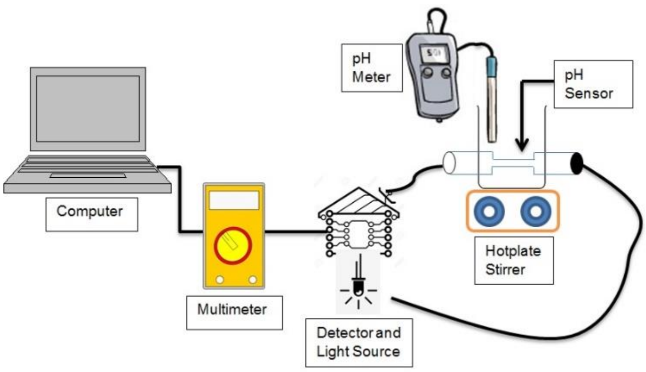

Figure 1. Instrumental set up for pH measurement

3. Result and Discussion
3.1. Preparation of Fiber Optic

Fiber optic was cut along 45 cm to minimize the light path length. The jacket and the cladding of fiber optic were removed for 5 cm length at designated area for placing sensitive pH materials. Fiber optic cables with and without jacket are shown at Figure 2a and Figure 2b respectively. Figure 2c shows the fire optic cable without jacket and cladding which is ready to be coated by pH sensitive material.

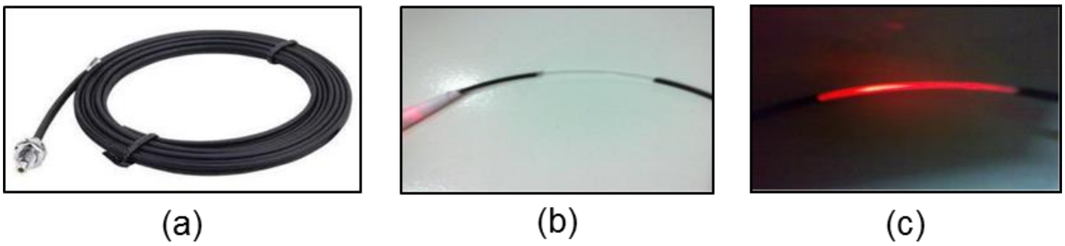

Figure 2. Fiber optic cable with jacket and cladding (a) without jacket (b) and without jacket and cladding (c)

Cleaning this designated area using ethanol and nitric acid before coating was to remove the organic and inorganic contaminants and also to activating the OH group from the surface of fiber optic core. This treatment is for strengthening the bond between Si molecule in TEOS and the O molecule from the fiber optic, while the bromophenol blue and cresol red were trapped in the porous glass film was formed from TEOS. This treatment also was performed to enhance the sensitivity of the fiber optic based pH sensor obtained. This step is very important to be done precisely. Removing of jacket and cladding are the success key to get the excellent connection between the fiber optic and the active material (bromophenol blue and cresol red).

3.2. Preparation of pH-sensitive Gel

The hydrolysis and condensation reactions were occurred during the preparation of the pH-sensitive fiber optic. Mixing TEOS with water will produce a colloidal solution. This involves hydrolysis reaction. OC_2H_5 molecules are replaced by hydroxyl group –(OH) as the following reaction:

$$(OC_2H_5)_3 - Si - OC_2H_{5(l)} + H_2O \rightarrow (OC_2H_5)_3 - Si - OH_{(aq)} + C_2H_5OH_{(aq)} \quad (1)$$

Then condensation reaction takes places so there was formation of dimer when the release of the water as the following:

$$(OC_2H_5)_3 - Si - OH_{(aq)} + (OC_2H_5)_3 - Si - OH_{(aq)} \xrightarrow{-H_2O} (OC_2H_5)_3 - Si - O(OC_2H_5)_{3(l)} \quad (2)$$

$$(OC_2H_5)_3 - Si - OH_{(aq)} + (OC_2H_5)_3 - Si - OC_2H_{5(l)} \xrightarrow{-C_2H_5OH} (OC_2H_5)_3 - Si - O(OC_2H_5)_{3(l)} \quad (3)$$

Basic concept of this sensor is when the light is directed to one end of the fiber optic, the light is transmitted through from one end to the other end of the fiber optic. Because some part of the cladding had been replaced by pH-sensitive material (described at section 2.2 and 2.3), partial absorption of the light will be occured when the light touches this material at the given wavelength. Part of the incoming Partially of light is absorbed into the film there because it interacts with the analytic material and the rest of incoming light that is not absorbed will be reflected back towards the core of fiber optic [36]. Due to the interaction of light with the analytic material causes the reflected light intensity is reduced, this optical signal will be guided back to detector.

3.3. Coating Fiber Optic with pH-sensitive Gel

After the first variation, the prepared fiber optic are then dipped into pH-sensitive gel. The process of dyeing is done for 5 minutes in a pH-sensitive gel that has been made for 3 times. The fiber optics are allowed to dry at room temperature and atmospheric pressure for 20 days in order to the process of evaporation occurs. The result is shown in this Figure 3, this proves that the sensor worthy to be tested. Before the test, at first the sensor is dyed in demineralized water.

Figure 3. Fiber optic dyeing result

3.4. Characterization of Fiber Optic pH Sensor

The 3 pieces of pH-sensor marked as A, B, and C is arranged as in Figure 3. Each sensor was tested 3 times. The measurement results of sensor A are shown in Figure 4. The response of the pH sensor A (A1) has the shape of the "S" curve corresponding to the Boltzmann sigmoidal function. Figure 4 shows that the addition of pH is followed by increasing of potential significantly. The measurement results of pH sensors A2 and A3 have the same pattern as that of the sensor A1. The measurement results of pH sensors B and C are shown in Figures 5 and 6, respectively. This indicates that all pH sensors have the same sigmoid curve pattern.

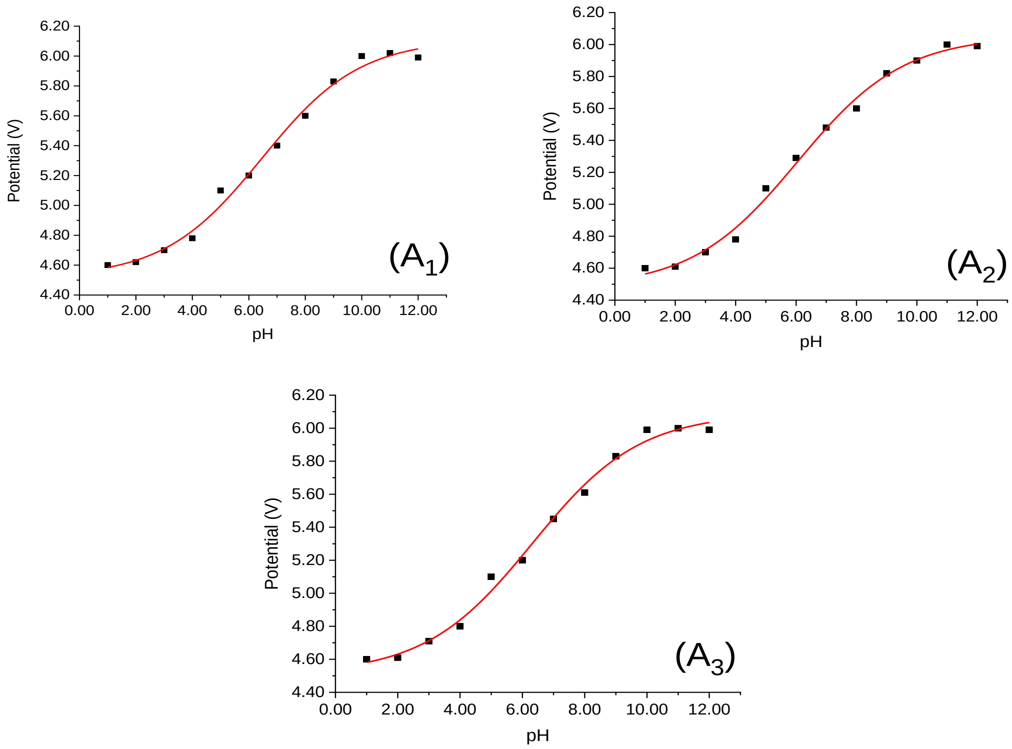

Figure 4. The first (A1), second (A2) and third (A3) measurements of the pH sensor A

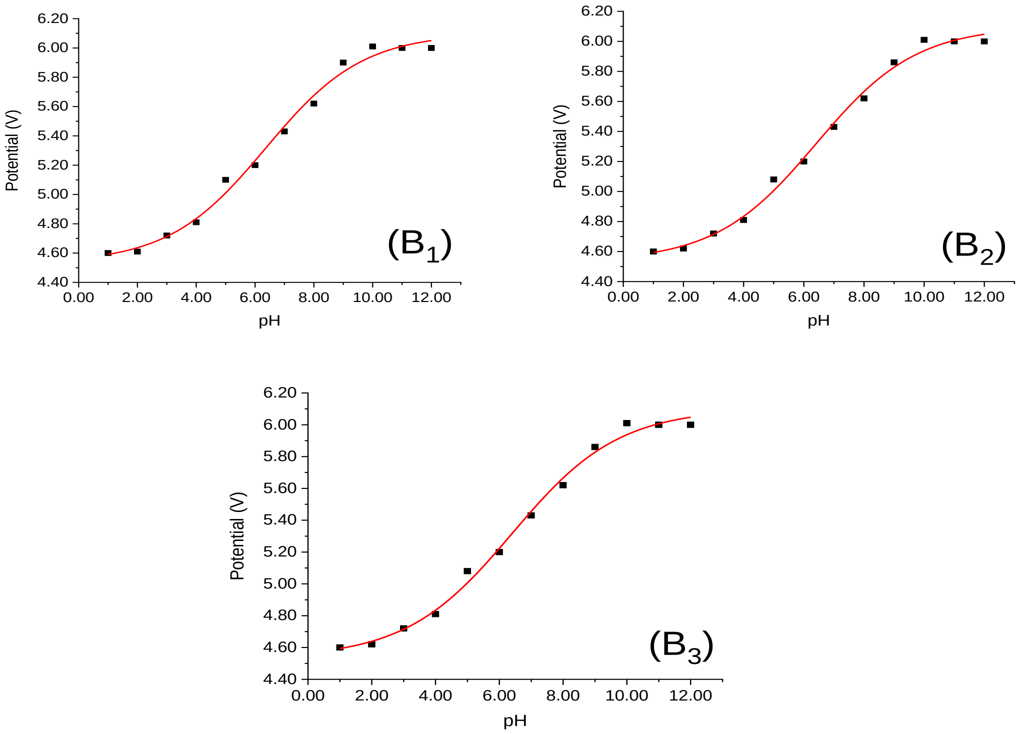

Figure 5. The first (B1), second (B2) and third (B3) measurements of the pH sensor B

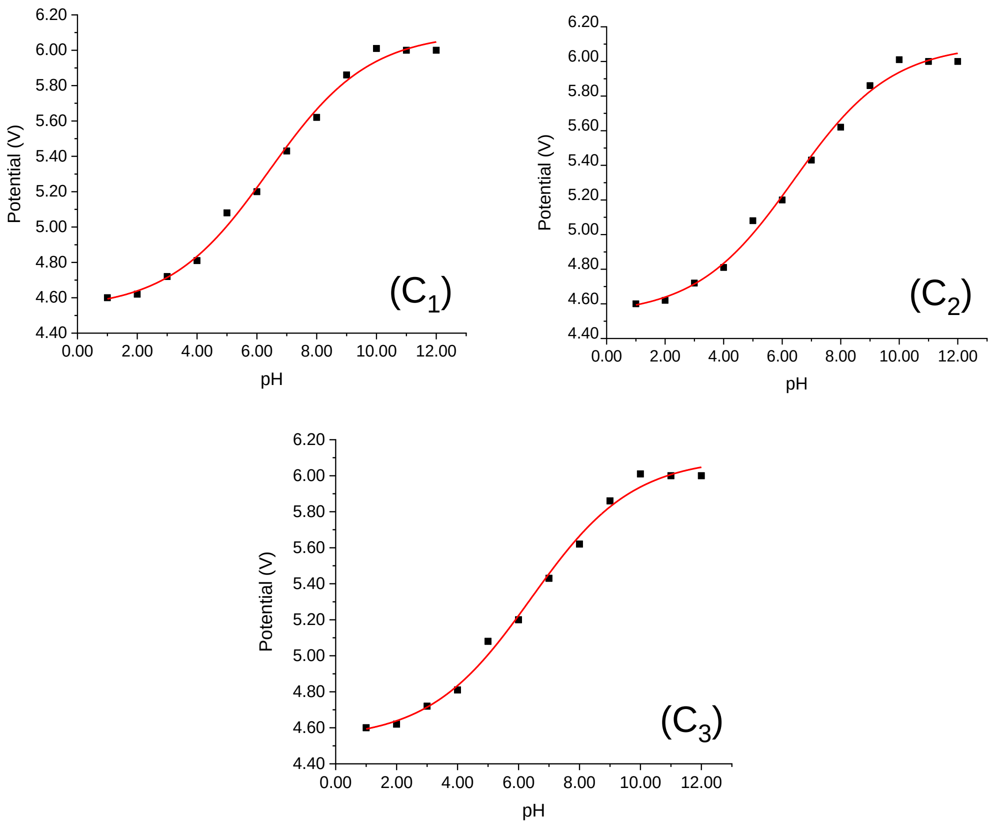

Figure 6. The first (C1), second (C2) and third (C3) measurements of the pH sensor C

3.5. Calibration range

Sensor's calibration range is the ideal condition of a system or instrument. Calibration of a sensor affects sensitivity of the sensor. In this work, we used sigmoid plot for calibration curve. The use of the sigmoid plot is based on the sensor response during pH measurement (as presented at Figures 4-6). A sigmoid function is mathematical function having a characteristic "S"-shaped curve and it often refers to the special case of the logistic function. In this study, each sensor was measured for 3 times. The all experiment was conducted from pH range 1.00 to 12.00. All regression value of calibration range are 0.99, which indicate very good correlation coefficient. The result shows that the sensor has a good sensitivity for pH measurement and work well in the large range of pH. The performance of several sensors for pH measurement are shown in Table 1. The comparison with other sensors indicates that pH sensor based on fiber optic coated bromophenol blue and cresol red has a better range for pH measurement. It means that the sensor can be used at broad range pH.

Table 1. Performance Comparison for Several Sensors

Sensor	pH range	Reference
Fluorescence based fibre optic pH sensor	10.00-13.20	[37]
pH sensor based on graphenic materials	4.00-10.00	[38]
pH sensor based on functionalized magnetic nanofluid	3.00-11.50	[39]
Printed flexible electrochemical pH sensors based on CuO nanorods	5.00-8.50	[40]
pH sensor based on fiber optic coated bromophenol blue and cresol red	1.00-11.0	This work

3.6. Anova Test

Anova test is used to test the distinction of average from 2 population or more (in the linear range, pH 4.50-11.00). If the value of IFI is smaller than on IFI critical, then there is no distinction significantly from the average result of measuring. While the value of IFI greater than on IFI critical, then there were differences from the average result of measuring. The result of anova test shown in Table 2. Table 2 indicates that the value of IFI in all various pH is smaller than IFI critical. It can be concluded that null hyphotesis (H_0) is accepted, which also means that the measurement data has an insignificant difference with 95% confidence interval. This result means that the sensor can work well to measure pH at widely range of pH.

Table 2. The Result of Anova Test

pH	IFI	IFI critical	Mark
pH 4.50 Sensor A,B,C	0.29897	5.14325	accepted
pH 5.00 Sensor A,B,C	1.60178	5.14325	accepted
pH 5.50 Sensor A,B,C	0.40027	5.14325	accepted
pH 6.00 Sensor A,B,C	0.28398	5.14325	accepted
pH 6.50 Sensor A,B,C	0.30250	5.14325	accepted
pH 7.00 Sensor A,B,C	0.40027	5.14325	accepted
pH 7.50 Sensor A,B,C	0.39178	5.14325	accepted
pH 8.00 Sensor A,B,C	0.21146	5.14325	accepted
pH 8.50 Sensor A,B,C	0.31899	5.14325	accepted
pH 9.00 Sensor A,B,C	2.33731	5.14325	accepted
pH 9.50 Sensor A,B,C	1.65374	5.14325	accepted
pH 10.00 Sensor A,B,C	0.03570	5.14325	accepted
pH 10.50 Sensor A,B,C	2.02091	5.14325	accepted
pH 11.00 Sensor A,B,C	1.57743	5.14325	accepted

4. Conclusion

The fiber optic coated bromophenol blue and cresol red has shown good performance as a novel pH sensor. The pH sensor based on fiber optic was prepared with two pH indicator (bromophenol blue and cresol red) simultaneously using sol-gel immobilization technique. The success key to get the excellent pH sensor are removing a jacket and cladding for great connection between the fiber optic and the active material (bromophenol blue and cresol red). The results obtained is the ratio between pH with potential. The pH sensor would provide a significant response to the pH range of 1.00±0.01 to 11.00±0.01. The result of measurement showed that the response of the pH sensor has the shape of the "S" curve corresponding to the

Boltzmann sigmoidal function. Testing of anova indicates that the sensor can work well at widely range pH.

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