

A Numerical Analysis of Various pH Level for Fiber Optic pH Sensor Based on Bromophenol Blue in Silica

M. Zolkapli, *Member, IEEE*, S. Saharudin, *Member, IEEE*, S. H. Herman, *Member, IEEE* and W. F. H. Abdullah, *Member, IEEE*

Abstract— The fabrication and characterization of an optical fiber pH sensor for the detection range 2 – 7 are described. The sensing element was prepared by coating the uncladded middle portion of a multimode plastic clad silica fiber (PCF) with xerogel film of immobilized bromophenol blue (BPB) prepared by a sol-gel process. The exponential decay of the evanescent wave at the core-cladding interface of the multimode fiber was utilized to determine the pH response. The objective of this work is to analyze the measurement of the fiber optic sensing probe towards various pH level. The intensity of the absorbance was analyzed using statistical technique (Statistical Package for the Social Sciences, SPSS) to identify the significant pH range that can be used as a reference in developing the sensor instrumentation in the future. pH2 shows the highest significance among all pH values based on the statistical results using error plots.

Index Terms— Evanescent wave, pH sensor, sol-gel, plastic clad silica fiber, absorption.

I. INTRODUCTION

In the past decades, tremendous efforts have taken place to enhance the performance of pH sensor which was widely used in various fields to monitor chemical and biological processes. Its applications ranged from chemical to biomedical, environmental as well as industrial monitoring. There are several methods of pH measurement developed viz. pH test strips, pH glass microelectrodes, indicator reagents, and other potentiometric devices to name a few. However, compared to traditional pH detective methods, optical fiber method is more appealing in view of its small size, electromagnetically immune, faster response and has the capability for multiplexing and remote sensing [1–4].

The sensing mechanism of fiber optic pH sensor is based on the incident light guided by the inner medium of the core to the active region of the optical fiber. It interacts with a chemical

indicator which alters the beam's intensity by absorption or fluorescence which is guided back to the detector. Thus, immobilization of the indicator on fiber is crucial for the development of optical pH sensor. Sol-gel process is a popular approach to immobilize the indicator dyes [5–8] in view of its simplicity and versatility. The process key parameters such as reactant formulation, catalyst, water content and reaction temperature can be exploited and adjusted to tailor the physicochemical properties of the film in order to optimize the sensor performances [9–11]. The process yields films that are tough, stable, inert, highly sensitive and intrinsically bind to the fiber core.

In the present study our approach is to study what is the reference pH using SPSS analysis for the sensing probe which sol-gel process was utilized to immobilize the BPB indicator on the PCF surface. The probe developed is structurally and optically characterized using field emission scanning electron microscope (FESEM), ultraviolet-visible (UV-vis) spectroscopy and spectrophotometry. We also report the spectral responses and calibration curves of the probe.

II. THEORY

An indicator dye dissolved in a solution has the following relationship:



$[H^+]$, $[I^-]$ and $[HI]$ represent the various concentrations. The acid dissociation equilibrium constant (K_a) for the indicator that describes this reaction is given by Eq. 2, in terms of the concentrations of the hydrogen ion, I^- and HI .

$$K_a = \frac{[H^+][I^-]}{[HI]} \quad (2)$$

Since we are working in aqueous solution, Eq.2 can be rearranged to Eq 3 and 4 by taking the negative base-ten logarithm of both sides and use the prefix "p" to denote the negative base-ten logarithm therefore $-\log K_a$ becomes pK_a and the $-\log[H^+]$ becomes pH. This leads to a very convenient way of writing the very small $[H^+]$ that occur in aqueous solution as numbers that generally fall between 0 and 14.

$$-\log(K_a) = -\log[H^+] - \log\left(\frac{[I^-]}{[HI]}\right) \quad (3)$$

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$$p(K_a) = \text{pH} - \log\left(\frac{[I^-]}{[HI]}\right) \quad (4)$$

If C is the total concentration and [HI], [I⁻] are the two relative concentrations of the dye solution, then

$$C = [HI] + [I^-] \quad (5)$$

The absorbance A of the solution, which is a function of the wavelength λ , is related to [HI] and [I⁻] as:

$$A(\lambda) = \alpha_\lambda^I [I^-] l + \alpha_\lambda^{HI} [HI] l \quad (6)$$

where α_λ^I is the molar absorption coefficient of the alkaline form and α_λ^{HI} is the molar absorption coefficient of the acidic form and l is the absorption length. The absorbance as a function of pH change as that species' concentration in solution changes. Hence, absorbance increases as pH increases.

III. EXPERIMENTAL WORK

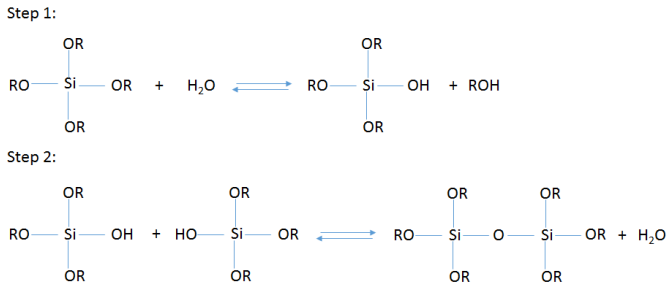


Fig. 1. Schematic representation of the two-step sol-gel method. Step1: hydrolysis and Step 2: condensation.

This section describes the preparation of the sensing fiber and sensitive matrix for the fabrication of optical fiber pH sensor. Sol-gel process is chosen since it is one of the most promising chemical strategies that provides simple solution with minimal operative conditions. The optically transparent glass like porous structure can be created at room temperature by a two-step acid or base catalyzed reaction involving hydrolysis and condensation. The metal alkoxide monomers (M(OR)₄) that act readily in water undergo hydrolysis to form silanols. Silanols are then link together to form siloxanes. Finally through condensation, silanols react with siloxanes to form porous sol-gel matrices after aging and drying processes under ambient atmospheres. The reaction scheme for such process is depicted in Fig. 1 [5, 9, 12].

A. Chemicals

Tetraethyl orthosilicate Si(OC₂H₅)₄ (TEOS) was purchased from Sigma-Aldrich. Ethanol (EtOH), hydrochloric acid (HCl), bromophenol blue (BPB) and triton X-100 were obtained from Merck KGaA, Germany. All reagents were analytical grade and used as received.

B. Preparation of The Sensitive Matrix

Tetraethylorthosilicate Si(OC₂H₅)₄ (TEOS) is used as the precursor liquid to prepare the pure silica thin film on fiber. A porous silica glass film with a refractive index of less than that of the fiber core ensures that the wave guidance condition is met. The silica sol was prepared by dissolving TEOS (99.999% Aldrich) in ethanol (EtOH) as TEOS is initially immiscible and require alcohol to form a homogeneous mixture. Then de-ionized water (DIW), HCl (0.1 M) and triton X-100 were added to the mixture to stimulate hydrolysis and prevent cracks in the sol-gel film. The composition of the prepared sol solution is as described in Table 1. The mixture was magnetically stirred for 1 hour at ambient temperature to obtain a stable silica sol. Bromophenol blue (BPB) was used as the pH indicator as it was readily available in the laboratory. The color changed from yellow to blue according to the pH which ranged from 3.0 to 4.6. The dye solution was prepared by dissolving BPB powder with EtOH and stirred under ambient temperature for 1 hour as described in Table 1. Both dye and sol mixture were then mixed followed by 2 hours of magnetic stirring at room temperature to ensure the formation of a yellowish sol-gel polymer. The synthesis scheme of the sol-gel is shown in Figure. 2.

TABLE 1. Composition of the Prepared Sol and Dye Solution.

| Sol solution | TEOS (mL) | EtOH (mL) | DIW (mL) | HCL (μL) | Triton X-100 (μL) |
|--------------|-----------|-----------|----------|----------|-------------------|
| | 15 | 25 | 12 | 160 | 80 |
| Dye solution | BPB (mg) | EtOH (mL) | | | |
| | 24 | 16 | | | |

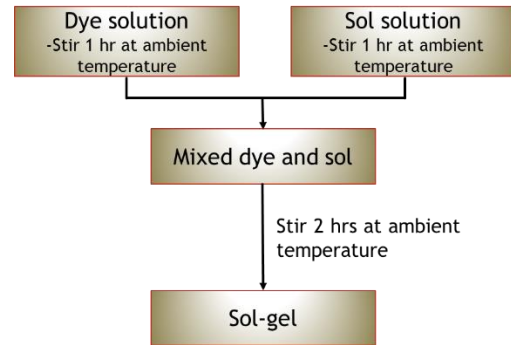


Fig. 2. Schematic representation of the two-step sol-gel method. Step1: hydrolysis and Step 2: condensation.

C. Preparation of The Sensing Fiber

A 21-cm length polymer clad silica multi-mode optical fiber with a core of diameter of 1000 μm and 1035 μm cladding is used in to fabricate the sensor. In order to reduce losses, both ends of the fiber were polished with diamond polishing film. Using a hot knife, a 10 mm length of central portion PCF cladding is removed to expose the core region for sol-gel coating. It was then wiped with acetone to ensure the cladding is completely removed. Prior to coating the uncladded surface was treated with 0.1 M NaOH for 24 hours

followed by thorough rinsing with de-ionized water and finally dried at room temperature for 1 hour. This cleaning procedure activates the hydroxyl groups on the surface which assists bonding of the sol-gel to the surface of the etched portion of the fiber [13, 14]. Finally, the dye-impregnated sol-gel was coated to the uncladded PCF fiber using a computer-controlled dip-coating apparatus at a speed of 400 mm/min. The thickness uniformity was controlled via the withdrawal speed [15]. These fibers were then kept for 14 days at atmospheric pressure and room temperature for stabilization of dyes in the host matrix which reduce the leaching of the dye molecules [16, 17]. Figure 3 shows the image of the prepared fiber with SMA connectors attached at both ends.



Fig. 3. pH sensitive fiber optic probe.

D. The Detection System Setup and Characterization

Figure 4 shows a schematic illustration of the experimental arrangement used to characterize the performance of the optical fiber pH sensor. In the sensing experiment, excitation is provided by a broadband fiber-coupled high power LED (Thorlabs, Inc., wavelength range is from 470 – 850 nm) driven by high-powered LED driver (DC2100, Thorlabs, Inc.) in pulse width modulation mode. The optical pH sensing system consists of a coated polymer clad silica fiber (Fujikura, core diameter 1000 μm) connected to the Avaspec multichannel fiber optic spectrometer (Avantes). A USB cable connects the spectrometer to a computer to display the spectral of the modulated light in the probe performance in various pH environments. FESEM was used to view its surface morphology. UV-vis absorption spectra for BPB sol-gel was measured by Jasco V670 UV-vis/ NIR spectrometer. The spectrum range employed was 300 – 800 nm with an accuracy of ± 0.3 nm.

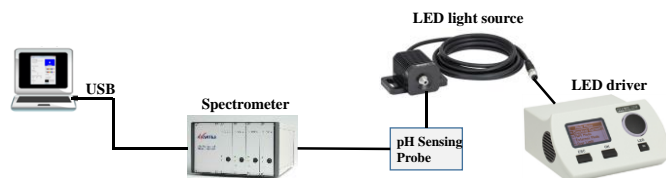


Fig. 4. Experimental setup to measure the spectral response of the fiber optic pH sensor.

E. Statistical Analysis

Data extracted from the spectrometer were then analyzed using statistical method. For this project, SPSS software was utilized as the statistical measurement tool in order to analyze the optical absorbance of the pH. The data were analyzed using the normality test and error plot. Normality test was used to determine whether a data set is well-modeled by a normal distribution or not, or to compute how likely an underlying random variable is to be normally distributed [18]. If the data set is normal or likely to be normal distributed, then further parametric tests are used for

conclusive findings. In this project, error bar plots is used to observe any population discrimination.

IV. RESULTS AND DISCUSSION

A. Characterization of Entrapped pH Indicator Matrix

Figure 5 shows the FESEM micrographs of BPB sol gel coated on a glass cover slip and PCF. These micrographs demonstrated that the indicator molecules are homogeneously diffused and well distributed inside the matrix supported by the presence of bromine in the EDX analysis as showed in Figure. 6. Bromine is a substance added to phenolsulfonphthalein to make BPB. This shows that the sol gel glass like film is covering the PCF surface. The surface of the dried sol gel on the glass cover slip showed less cracks compared to the dried sol gel on PCF. Factors that could cause films to crack include rapid shrinkage during drying and evaporation of liquid by-products of condensation reaction, unclean surface of the substrate and high viscosity of the sol. To overcome cracked surfaces drying has to be carried out gradually at lower temperature and reduce the thickness of the film by characterizing the optimum withdrawal rate [10, 18].

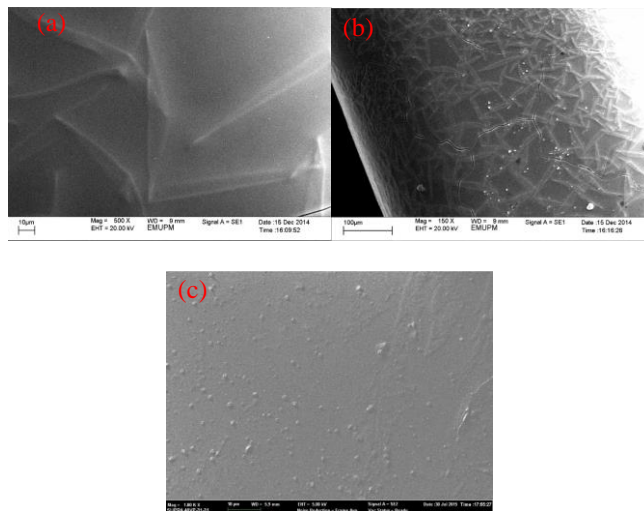


Fig. 5. FESEM images of BPB sol gel coated on polymer clad fiber (a) at 500x magnification, (b) at 150x magnification and (c) on cover slip glass at 1000x magnification.

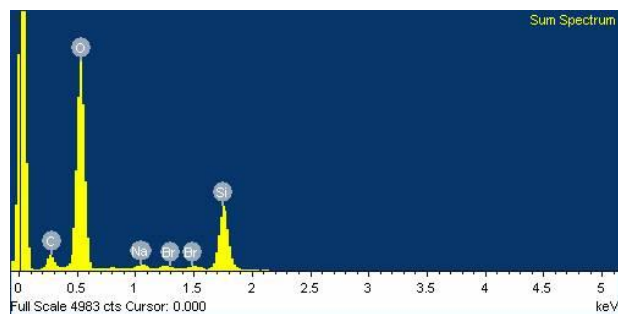


Fig. 6. FESEM images of BPB sol gel coated on polymer clad fiber (a) at 500x magnification

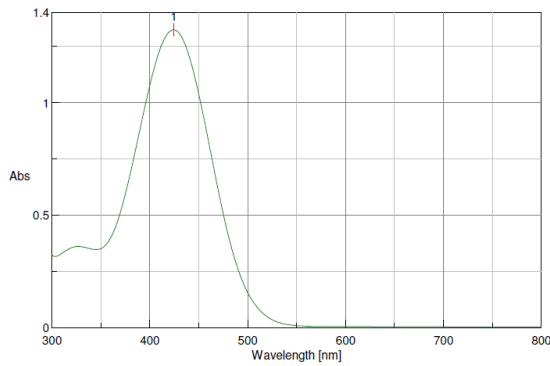


Fig. 7. Absorption spectrum of BPB sol-gel in cuvette glass.

B. Optical Properties of BPB Immobilized Sol-gel

Figure 7 represents the absorption spectrum of BPB sol-gel in cuvette glass. As shown, the absorption band is observed in the visible region which peaks at 424 nm. Hence, the results of the BPB sol-gel when coated on PCF is expected to be within a similar range when function as the sensing probe.

C. pH Sensing Analysis

Absorption spectra of the tested indicator measured for different pH values showed absorption bands which could be attributed to basic and acidic forms of the indicator. Fig. 8 shows the variation in output intensity of the dissolved BPB sol gel at different pH value of the solution. It is evident that absorbance intensity varies over the pH sensing range from 2 to 7 and likewise for the colour of the sol-gel. The peak of the absorbance increases as the pH value increase. The colour variation in different pH is due to the reaction of the hydroxyl ions that freely penetrate into the matrix with the indicator. The variation in colours is shown in Figure. 9.

Figure 10 shows the variation in output intensity of the wide range fiber with a change in the pH value of the solution surrounding the sensing region. It is evident from the spectrum that the absorption band of the acidic form is in the region of 470 nm while the basic form in the region of 590 nm. Isosbestic point is observed at 520 nm. This is where the spectra crosses and the absorbance of the reaction mixture at this wavelength remains invariant, regardless of the extent of reaction. As the pH increases, the absorbance increases as well. The absorbance of BPB sensitive film varies almost linearly for pH range 2 – 4 with an equation of

$$A = 0.0115pH + 0.0116 \quad (1)$$

while the coefficient of determination (R^2) is 0.996. Absorbance were also measured at pH value lower than 2 and higher than 4. However, the absorbance appeared to reduce or even disappeared which indicated that the film loses its efficacy when the pH of the solution is lower than 2 and higher than 4. Hence measurement in strong acid and alkaline condition is not suitable and different dye is needed.

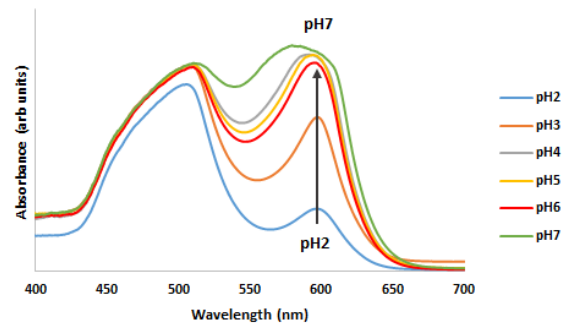


Fig. 8. Spectrum of dissolved BPB sol gel at different pH range 2-7.

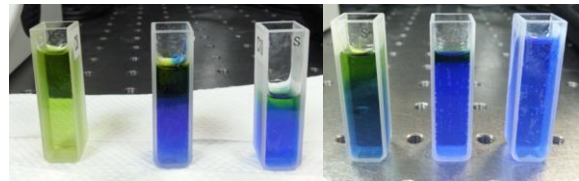


Fig. 9. Variations in colour of entrapped BPB in silica matrix in different pH solutions.

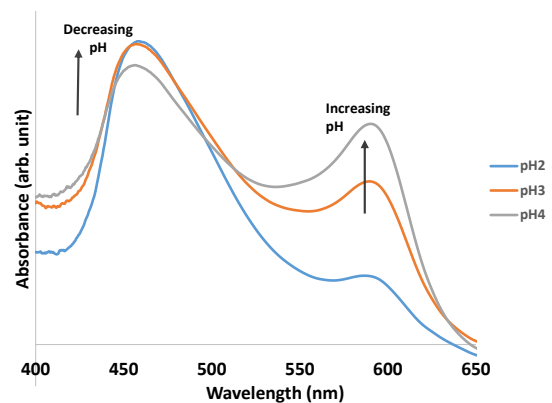


Fig. 10. Spectrum of immobilized BPB sol gel on PCF for pH range 2-4.

A test on reversibility of the sensitive sol-gel film was also carried out. It was evaluated by neutralizing the probe after each pH test before immersing the probe in another pH value. The test was carried out in pH 2 - 4 as the response is more linear in this range as discussed earlier. The response is depicted in Figure. 11 and it demonstrates that the response of the film is fully reversible as it goes back to the reference point after being neutralized with maximum deviation for pH 4 and 2 is of less than 0.018 for both acid and basic form.

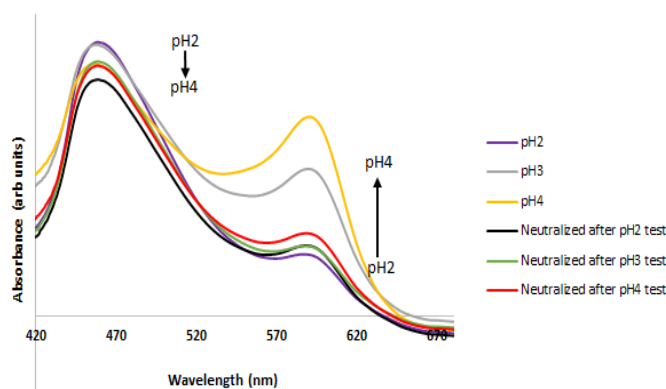


Fig. 11. The reversibility of the sensor when neutralized after testing in different pH value.

D. SPSS Analysis

The outcomes of the normality tests applied to all the data sets, are then being recorded and analyzed as shown in Table 2. Measurement outcomes by the Kolmogorov-Smirnov (K-S) and Shapiro-Wilk tests have produced significant p -values from a minimum of 0.2 to a maximum of 0.983. The rule for normal distribution is if the Sig. p -value for both Kolmogorov-Smirnov and Shapiro-Wilk tests is greater than 0.05, then the data set implies having normal distribution and the data is valid for next analysis for error bar. Otherwise, if it is below than 0.05, then the data significantly deviate from a normal distribution form [18].

TABLE 2. Normality test of pH

| | Kolmogorov-Smirnov ^a | | | Shapiro-Wilk | | |
|-----|---------------------------------|----|-------|--------------|----|------|
| | Statistic | df | Sig. | Statistic | df | Sig. |
| ph2 | .083 | 50 | .200* | .979 | 50 | .509 |
| ph3 | .074 | 50 | .200* | .992 | 50 | .983 |
| ph4 | .078 | 50 | .200* | .984 | 50 | .733 |

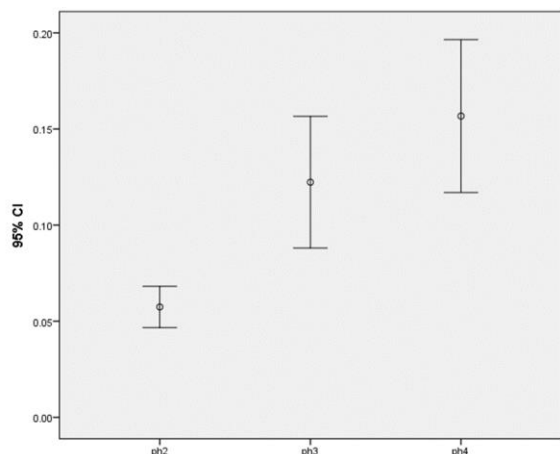


Fig. 12. Error bar plot.

Figure. 12 shows the error bar with regards to the pH of the solutions. It can be clearly seen that, among the three pH values, only pH2 can be discriminated between each other since there is no overlapping of data compared to pH3 and pH4. However, for pH3 and 4 the difference between the two

means is not statistically significant. As a result, this test was able to prove that pH2 show the highest significance among all pH values hence can be selected to be the reference of this sensing probe for development of sensor instrumentation in the future.

V. CONCLUSION

The study has successfully demonstrated an absorption-type optical pH sensitive film based on immobilized BPB in sol-gel film. Characterization of the sensor was performed using a simple optical setup based on a single wavelength measurement. The BPB sensitive film linearly responds over a pH range of 2 - 4 and is reversible with maximum deviation of less than 0.018 for both acid and basic form. EDX analysis and FESEM microscopy respectively showed homogeneously diffused indicator molecules and film surface with minimum cracks. These data adequately substantiate that the pH indicator and BPB can be immobilized in matrices of porous silica using the sol-gel technique and in designing the sensor, pH2 can be selected to be the reference of this sensing probe for development of sensor instrumentation in the future. In conclusion, it is feasible to develop a polymer clad silica fiber for pH sensing using a simple, low cost technique which can be tailored for many special applications.

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CONFLICTS OF INTEREST

The authors declare that there is no conflict of interest regarding the publication of this article. The funding sponsors had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, and in the decision to publish the results.

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