Evanescent wave absorption based fiber optic pH sensor prepared by dye doped sol-gel immobilization technique

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Abstract

A fiber optic pH sensor based on evanescent wave absorption is presented. To prepare the probe a small length of the cladding is removed from the middle portion of the fiber. A thin porous film of glass with pH-sensitive dye entrapped in it is deposited on the surface of the unclad portion of the fiber using sol-gel technology. The sensor response and its dynamic range are reported for phenol red, cresol red and bromophenol blue dyes. The sol-gel process has been found to increase the dynamic range of the pH sensor.

Keywords: Fiber optics; Sensor; Evanescent wave; Absorption; pH; Sol-gel process

1. Introduction

In the recent years there has been a remarkable progress in the development of fiber optic sensors for the detection of various chemicals [1–7]. The most investigated chemical parameter is the pH of the fluid. This is because continuous monitoring of pH is required in practically all kinds of sciences including chemical, biomedical and environmental. Fiber optic pH sensors have the advantage of very small size, flexibility and offer an attractive possibility for invasive analysis of plants and animal tissues. A fascinating feature is the remote sensing. Further, in fiber optic sensors the signal is optical therefore there is no electromagnetic interference and hence no risk of fire or spark. The first fiber optic pH sensor based on dye chemistry was developed by Peterson et al. [8]. Since that time a number of fiber optic pH sensors employing different optical or spectroscopic phenomena have been reported [9–16]. The phenomena used are bulk absorption, optical reflectance, fluorescence and energy transfer.

In this paper we report a fiber optic pH sensor utilizing the evanescent wave absorption. The fiber optic sensors based on evanescent wave absorption have been extensively studied for the detection and the measurement of the concentration of an absorbing fluid [17–22]. In this type of sensor, cladding is removed from the middle portion of the fiber and is replaced by an absorbing fluid. When the light is launched into the fiber the absorption of the evanescent field penetrating into the unclad region takes place. The presence of the fluid and its concentration are determined by measuring the fractional change in power at the other end of the fiber. One of the main advantages of the fiber optic evanescent wave absorption sensor is the possibility of distributed sensing. The pH sensor developed in our laboratory is based on the immobilization of the pH-sensitive dye on the surface of the unclad core of the fiber. It works on the evanescent wave absorption phenomenon but it is different from the one mentioned above in the sense that in this case light interacts with analyte (i.e. H⁺ ions) through a dye immobilized on the surface of the fiber core. The absorbance of the dye depends on the pH of the fluid surrounding the coated region of the fiber. There are many methods for immobilizing the dyes on the surface of the core. We have used the sol-gel process for preparing a
A 40 cm of plastic clad silica (PCS) fiber of 600 μm core diameter with 0.17 numerical aperture and 1.457 core refractive index was used for the fabrication of the pH sensor. A large core diameter fiber was used for the sensor because of the following reasons: (a) light coupling is easier, (b) because of large surface area of the core the film can adhere easily, and (c) the fiber handling is easier. The jacket and the cladding of the fiber were removed mechanically from 5 cm length of the middle portion of the fiber. This was followed by cleaning of core in acetone. To adhere the film on the surface of the core the OH groups on the silica core were activated by an acid treatment. These OH groups activated on the surface form bonds with the silica molecules in the porous glass film and help thin film to adhere to the fiber core surface. To activate OH groups the unclad fiber was first washed with a soap solution and then treated with 30% HNO₃ for 5 min. The unclad portion of the fiber was then washed with deionized water of pH less than 7. The final step was its cleaning with acetone.

Thin film of glass on the core of the fiber was prepared by sol-gel technique and dip coating method. In dip coating method the unclad fiber is first lowered into the still coating solution and then it is pulled at a definite speed. The thickness of the film depends on the pulling speed. In sol-gel technique the glasses are prepared from the hydrolysis and condensation polymerization of a metal alkoxide solution followed by the densification process at low temperature. The low temperature enables to use a wide range of dyes of low thermal stability. The precursor liquid used for preparing the pure silica thin film on the fiber core was tetraethyl orthosilicate (TEOS). This was used because the refractive index of the porous silica glass film produced is less than the refractive index of the fiber core thus allowing the wave guidance condition to be satisfied. Three coating solutions corresponding to three different dyes, namely phenol red, cresol red and bromophenol blue, were prepared. In all the solutions 30 ml of TEOS, 30 ml of anhydrous ethanol and 2 ml of deionized distilled water along with a suitable amount of dye were mixed in the room temperature. The amount of dyes mixed were 43 mg phenol red, 46 mg cresol red and 82 mg bromophenol blue. This gave us three solutions of different dyes but with the same concentration. After mixing all the three solutions were stirred for 30 min at 60°C. The unclad fibers prepared for coating were then dipcoated at a pulling speed of 10 cm/min. This gave a film thickness of about 0.15 μm. After coating, the fibers were dried at atmospheric pressure and room temperature for 20 days. These fibers were then immersed in water to allow the excess and unbound dye to be removed.

The experimental arrangement used to characterize the pH sensor is shown in Fig. 1. Light from a tungsten halogen lamp was launched into a coated fiber mounted in a cylindrical glass cell with the help of a circular slit and a microscope objective of numerical aperture 0.4. The coated portion of the fiber was kept in the middle of the cell. The other end of the fiber was connected to a powermeter (Newport 1825-C) to measure the transmitted power. The cell was filled with deionized water and was kept on a magnetic stirrer. To measure the pH of the water a pH electrode was introduced in the flow cell. The pH of the water was increased by adding NaOH solution. To decrease its pH, HCl was used. Interference filters of different wavelengths were introduced between the lamp and the microscope objective to scan the maximum fractional change in transmitted power over the entire pH range.

Before evaluating the response characteristics and the dynamic pH range, the optimum sensing wavelength of the light was investigated. For this the transmitted powers were measured corresponding to very low and very high
Fig. 2. Calibration curve of the fiber optic pH sensor prepared by the immobilization of phenol red dye on the surface of the fiber core using sol-gel process.

pH of the water for wavelengths ranging from 500 nm to 700 nm in an interval of 20 nm. From these measurements the fractional change in transmitted power over the whole pH range was calculated for all wavelengths scanned. The wavelength which gives the maximum fractional change in power was used as the optimum sensing wavelength. This exercise was carried out for all the dyes used. It was found that the optimum wavelengths for phenol red, cresol red and bromophenol blue lie in the range 610 nm to 630 nm. Therefore, an interference filter of 620 nm wavelength was used for all the three dyes in the experimental set up to study the sensor response and the dynamic range.

Fig. 2 shows the variation of normalized power recorded as a function of pH for the sensor based on phenol red dye. As the pH of the water around the coated core increases the power transmitted decreases. It may be noted that the modulation in power transmitted occurs in the pH range 7.5 to 11.5. The phenol red in water has peak absorption around 570 nm and its absorbance changes in the pH range of 6.5 to 8.0. It means that in porous glass matrix, a shift in peak absorption wavelength and an increase in the pH dynamic range of the dye take place. The response time of the sensor was measured by changing the pH of the water in a step from 7.0 to 12.0 and it was found to be approximately 5 s.

Fig. 3. Same as Fig. 2 except that in this case the dye immobilized is cresol red.

Fig. 4. Same as Fig. 2 except that in this case the dye immobilized is bromophenol blue.

In Figs. 3 and 4, the normalized power recorded as a function of pH have been plotted for cresol red and bromophenol blue dyes respectively. The results are similar to those obtained for phenol red. The difference occurs in the dynamic pH range. For cresol red the dynamic pH range is from 6.5 to 11.0 while in the case of bromophenol blue it is from 4.0 to 7.5.

The fiber optic pH sensor described above has many advantages. First, the pH equilibrium of the test fluid is not affected by the probe because the signal is optical and not electrical. Second, since a very small amount of pH sensitive dye is immobilized, it does not change the pH equilibrium of the fluid even if the probe is kept for a long time in the fluid. Therefore, the pH of the fluid can be monitored continuously without a break unlike the pH electrode. Third, the pH sensor based on evanescent wave absorption and described above can be used for distributed sensing. This can be done by coating a required length of the fiber core along which the pH variation to be measured. The measurements along the fiber can be carried out using OTDR technique. For point sensing, the probe can be prepared by removing a small length of the cladding from one of the ends of the fiber and then coating with the dye using sol-gel technology. The endface is made reflecting.

In summary, we have presented a fiber optic pH sensor based on evanescent wave absorption. The probe is prepared by immobilizing a pH-sensitive dye on the surface of the fiber core using sol-gel technology. To study the sensor response and the dynamic range of the sensor three dyes are used. The sol-gel glass films produced on the surface of the core with pH sensitive dye entrapped have been found to increase the dynamic pH range of the sensor.

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References