Fabrication and characterization of U-shaped fiber-optic pH probes

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Abstract

Fabrication and characterization of U-shaped fiber optic pH probes utilizing evanescent field absorption spectroscopy and dye doped sol-gel immobilization technology are presented. The U-shaped probe is used to increase the evanescent field in the film and hence its interaction with the dyes present in the film. The influences of bending radius of the probe and the numerical aperture of the fiber on the sensitivity of the sensor are studied. It has been shown that, for a given pH, as the bending radius of the U-shaped probe decreases the sensitivity of the sensor increases. Further, for a given bending radius and the fiber core diameter, increase in the numerical aperture of the fiber increases the sensitivity of the pH sensor. The response time of the sensor reported in the present study is approximately 15 s.

Keywords: Optical fiber; Sensor; pH; U-shaped probe; Sol-gel; Sensitivity

1. Introduction

The measurement and control of pH is required in practically all kinds of sciences including chemical, biomedical and environmental. Potentiometric techniques employing a pH sensitive membrane such as glass membrane electrodes are commonly used for pH measurement. In recent years, numerous efforts have been directed toward the development of fiber optic pH sensors. This is because fiber optic pH sensors offer many advantages over other types of sensors. In particular, these are perceived as being safer for in vivo use since the signal is optical and there is no electromagnetic interference. Further, remote sensing can be achieved using optical fibers because the signal can be carried over a long distance. Since optical fibers avoid cross-talk, a small and compact multi-sensing fiber optic probe is possible.

Optical fiber pH sensors are based on pH-induced reversible changes in optical or spectroscopic properties such as absorbance, reflectance, fluorescence, energy transfer etc. The major component in an optical fiber sensor is a pH sensitive layer/film that is prepared by immobilizing a pH sensitive dye onto the tip or sides of an optical fiber. To immobilize, many research groups have used either covalent chemical linking or simple physical encapsulation techniques. For covalent linking of the dye molecules surface modification is required [1-3]. The covalent linking method is a long, complex and tedious method and may lead to loss of dye sensitivity or result in poor absorption and fluorescence properties [4]. In the non-covalent immobilization techniques, the dye is immobilized on the polymer support and entrapped behind semi-permeable membranes [5-7]. The disadvantage of the non-covalent immobilization methods is that these suffer from leachability of the dye that makes the long term use of the sensor impractical. Recently, sol-gel technology has been developed for the immobilization of pH-sensitive dyes [8-13]. In this technique, a thin film of glass with dye entrapped in it is prepared from the hydrolysis and condensation polymerization of a metal alkoxide solution followed by the densification process. The sol-gel technology has several advantages over other methods of film deposition. Apart from simplicity, the film produced is tough, inert and more resistant than polymer films in aggressive environments. Most of the fiber optic pH sensors developed and reported in the literature have 3-4 pH unit dynamic range. Recently, Gupta and Sharma [13] reported a long-range fiber optic pH sensor based on evanescent wave absorption spectroscopy. The probe was prepared by immobilizing a mixture of three suitably selected pH-sensitive dyes on the surface of the unclad core of the fiber using sol-gel technology. Due to the mixture of dyes, the dynamic range of the sensor increased to 8-9 pH unit. In the present paper, we report the fabrication and characterization of a fiber optic pH sensor based on U-shaped probe. The U-shaped probe as an evanescent wave absorption sensor has been shown to possess high sensitivity as
The additional advantage of U-shaped probe is that it can be used as a point sensor and is less fragile as compared to tapered probe. The effects of bending radius of the probe and the numerical aperture of the fiber on the sensitivity of the pH sensor have been studied.

2. Experimental

2.1. Probe fabrication

Plastic clad silica fibers (PCS) of 600 mm core diameter and numerical apertures (NA) 0.17 and 0.40 with same refractive index of the material of the core were used for the fabrication of the U-shaped probes. The probes were fabricated according to the method described in [14,16]. The method of preparing a thin film of glass on the fiber core using sol-gel technology was slightly modified from our previous studies [11,13]. The modification was carried out to make the film hard and more stable on the core of the fiber. Similar to our previous studies tetraethyl orthosilicate (TEOS) was used as the precursor liquid. To prepare the coating solution, 30 ml of TEOS, 30 ml of anhydrous ethanol, 2 ml of deionized distilled water, 2.5 ml of 2-methoxy ethanol and 1 ml of HNO3 along with 46 mg cresol red, 82 mg bromophenol blue and 42 mg chlorophenol red were mixed at room temperature. These dyes were selected because the mixture of these dyes gives a large pH range. After mixing, the solution was stirred for 5 h at 60 °C. The unclad U-shaped probes of different bending radii and numerical apertures were dip-coated at a pulling speed of 10 cm/min. The coated fibers were then dried at 200 °C for 4 h. These probes were then immersed in water to allow the excess and unbound dyes to be removed from the film.

2.2. Apparatus

The experimental arrangement used to characterize and study the sensitivity of the U-shaped pH probes is shown in Fig. 1. Light from a tungsten halogen lamp was launched into the coated U-shaped fiber optic probe mounted in a cylindrical glass cell with the help of a circular slit and a microscope objective of 0.65 numerical aperture. An interference filter of 600 nm wavelength was introduced between the slit and the microscope objective to achieve maximum fractional change in transmitted power per unit change in pH [13]. The other end of the fiber probe was connected to a detection system. The cell was filled with deionized water and was kept on a magnetic stirrer. The pH of the water was varied on adding HCl or NaOH solution in the cell. To measure the pH and hence to calibrate the sensor, a pH electrode was introduced in the glass cell.

3. Results and discussion

To characterize the U-shaped fiber optic pH probes, the experiments were carried out on three probes of bending radii 3.48, 1.14 and 0.82 mm fabricated from the PCS fiber of numerical aperture 0.40. The transmitted power was measured corresponding to different pH values of water in the glass cell. Fig. 2 shows the variation of normalized power recorded as a function of pH of the water around the coated U-shaped probe. The results have been plotted for the probes of different bending radii. These measurements were carried out both for increasing and decreasing pH value and were repeated a number of times for 2 weeks. Each time an almost reproducible response was obtained. Similar to our previous study on straight fiber probe [13], the modulation in transmitted power starts around pH 4.0. It may be noted that the probe with large bending radius has small variation. In the case of probe with 0.82 mm bending radius the variation is large and it covers almost full range of the normalized output power in the pH range 4-13. The decrement in the transmitted power is about 80% up to pH 12.0. The decrement in the transmitted power in our previous study on straight probe with 5 cm length was about 50% up to the same pH [13]. Thus, the present U-shaped probe with 0.82 mm bending radius is highly sensitive. Fig. 3 shows the variation of normalized power as a function of pH for the probe with bending radius 1.62 mm fabricated from the fiber.
of numerical aperture equal to 0.17. It may be noted that the variation is similar to those reported in Fig. 2. This suggests that the change in numerical aperture of the fiber does not affect the behavior of the response curve of the sensor.

Fig. 4 shows the pH dependence of the sensitivity of the U-shaped probe with bending radius equal to 0.82 mm fabricated from the fiber of numerical aperture equal to 0.40. The sensitivity of the sensor has been defined as the fractional change in the transmitted power per unit change in pH of the water \( \frac{\Delta P}{P} \frac{dP}{d\text{pH}} \). It may be noted that the sensitivity of the probe increases as the pH increases. In Fig. 5 we have shown the effect of bending radius on the sensitivity of the probe fabricated from the fiber of numerical aperture equal to 0.40 for the pH around the probe equal to 8.0. It may be noted that as the bending radius decreases the sensitivity of the probe increases. This is because as the

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**Fig. 2.** Calibration curve of the fiber optic pH sensor for the U-shaped probes of bending radii 0.82, 1.14 and 3.48 mm and the fiber of numerical aperture 0.40.

**Fig. 3.** Calibration curve of the fiber optic pH sensor for the U-shaped probe of bending radius 1.62 mm and the fiber of numerical aperture 0.17.

**Fig. 4.** Variation of sensitivity with pH for the U-shaped probe of 0.82 mm bending radius.
bending radius decreases, the evanescent field in the film increases and hence the absorption of light in the film increases. To see the effect of numerical aperture of the fiber on the sensitivity of the probe, the sensitivity of the U-shaped probe with bending radius equal to 1.62 mm and fabricated from the fiber of numerical aperture equal to 0.17 has also been marked in Fig. 5. It may be seen that for the same bending radius and pH of the water the probe fabricated from the fiber of numerical aperture equal to 0.17 is less sensitive than that fabricated from the fiber of numerical aperture equal to 0.40. These results are consistent with the theoretical results reported by Gupta et al. [14]. Thus one should prefer fiber of high numerical aperture for fabricating the pH probe.

We have also measured the response time of the pH probe. To measure, the probe with bending radius equal to 1.14 mm and fiber numerical aperture equal to 0.40 was dipped in a buffer solution of pH 4.0. After initial change in output power, no further change was observed in output power till 20 s. The probe was then quickly dipped in buffer solution of pH 9.0. A change in output power was observed and the variation was measured with time. After 15 s of dipping the output power became constant as shown in Fig. 6. This suggests that the response time of the pH sensor is about 15 s.

The fiber optic pH sensor based on U-shaped probe has many advantages. The most important is its high sensitivity as shown above. It is small in size, easy to fabricate and is less fragile as compared to tapered probe. The U-shaped probe can be used as a point sensor. Further, it can be used for quasi-distributed sensing by fabricating and coating U-shaped probes at different locations in the same PCS fiber. The measurements for quasi-distributed sensing are
carried out using OTDR technique. In fact, Kvasnik and McGrath [17] have carried out investigations on multipoint quasi-distributed optical fiber chemical sensors utilizing the evanescent field absorption phenomenon and have shown the viability of implementing distributed evanescent field absorption sensors.

In summary, the fabrication and characterization of a U-shaped fiber optic pH sensor based on evanescent wave absorption and sol-gel immobilization technique have been carried out. The effects of bending radius of the probe and the numerical aperture of the fiber on the sensitivity of the pH sensor have been studied. The sensitivity of the probe increases with the decrease in the bending radius of the U-shaped probe. It can further be increased if the probe is fabricated from the fiber of high numerical aperture. The response time of the sensor is about 15 s.

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References


Biographies

B.D. Gupta received his BSc (Hons.) (1973) and MSc degree in physics (1975) from Aligarh Muslim University (India) and a PhD degree in physics (1979) from the Indian Institute of Technology, New Delhi. In 1978 he joined the Indian Institute of Technology, New Delhi, where he is currently an assistant professor of physics. Dr. Gupta has also worked at the University of Guelph (Canada) during 1982-1983, the University of Toronto (Canada) in 1985, and the Florida State University (USA) in 1988. In 1993, he visited the Department of Electronic and Electrical Engineering at the University of Strathclyde (UK) to work on fiber optic chemical sensors under the Indo-British Fibre Optics Project. In 1992, he was awarded the ICTP Associateship by the International Center for Theoretical Physics, Trieste (Italy), which he held for eight consecutive years. In this capacity, he visited ICTP (Italy) in both 1994 and 1996. Dr. Gupta is a recipient of the 1991 Gowri Memorial Award of the Institution Of Electronics and Telecommunication Engineers (India). He has published more than 40 research papers including 3 review articles. Dr. Gupta is the co-editor of the Proceedings of SPIE Vol. 3666 (1999). His current area of interest is fiber optic sensors. He is a life member of the Optical Society of India and the Indian Chapter of ICTP.

Navneet K. Sharma received his MSc degree in physics (1997) from Roorkee University (India). Mr. Sharma was a lecturer in Government Polytechnic, Manesar in 1998. Since July 2000, he is a full-time PhD student at the Indian Institute of Technology, Delhi. Mr. Sharma has been selected for UGC (India) Lectureship in 2000.