A sensitive fibre optic pH sensor using multiple sol–gel coatings

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Abstract
The fabrication and characterization of a fibre optic pH sensor based on
evanescent wave absorption is presented. The unclad portion of a
multi-mode optical fibre is coated with a pH sensitive dye, which is
immobilized by the sol–gel route. The sensitivity of the device has been
found to increase when multiple sol–gel coatings are used as the sensing
region. The dynamic range and the temporal response of the sensor are
investigated for two different dyes, namely bromocresol purple and
bromocresol green. The performance of the device is evaluated in terms of
the results obtained during actual measurements.

Keywords: Fibre optics, optical fibre, evanescent wave, sensor, pH, sol–gel,
absorption, multi-layer

1. Introduction

One of the most commonly monitored chemical parameters of
a fluid is its pH value. Different types of pH sensors, such as
indicator strips, pH electrodes, etc, are now easily available
and commercially used. Recently, fibre optic based pH
optrodes have been designed and these are finding their unique
use, especially for *in situ* and *in vivo* measurements [1–3].
Such optrodes are frequently used in all kinds of hazardous
environments, such as deep-water analysis, chemical reactors
or wastewater monitoring. Fibre optic pH sensors have many
advantages over conventional pH sensors. They are small,
immune to electromagnetic interference and have remote
sensing capability, among other desirable features. A notable
advantage is that they do not require a reference electrode for
the pH measurement. Most of the fibre optic pH sensors are of
the intrinsic variety. Different portions of the optic fibre can
be used for sensing, such as the end face or the core–cladding
interface. Also, various phenomena such as absorption,
reflection or fluorescence can be exploited for the sensor
fabrication. The use of optical absorption at the core–cladding
interface has paved the way for a different class of sensors
known as evanescent wave fibre optic sensors (EWFS) [4, 5].

Within the last decade, the sol–gel route opened up new
possibilities for the fabrication of fibre optic sensors (FOSs) [6,
7]. The sol–gel technique essentially relies on a process
involving a solution or sol that undergoes a sol–gel transition.
It is used to prepare glasses and ceramics at low temperature,
which is done by the hydrolysis and polymerization of organic
precursors followed by room temperature curing [8–11]. Apart
from simplicity, the films produced by this sol–gel process
are tough, inert, intrinsically bound to the fibre core and
more resistant than polymer films in aggressive environments.
Similar to the polymeric support, the indicator phase is
confined within a tubular membrane, which is permeable to the
analyte (the hydrogen ions in this case). Since the indicator and
the analyte are in the same phase the response time of the sensor
is very small. The sensitivity of some of the recently developed
fibre optic pH sensors, using the sol–gel route, has been found
to be low, as there is only a 20% fractional change in output
intensity when a single dye is used [12]. So in order to enhance
the sensitivity, we propose a new method, called the multiple
sol–gel coating technique. In this technique, different layers of
sol–gel thin films containing the pH sensing dye are coated one
over the other on the unclad region of the fibre. The sensitivity
of the device is found to increase by 70% when multi-layer sol–

gel coatings are employed. The dynamic range and temporal response of the sensor are investigated for two dyes, namely bromocresol purple (BCP) and bromocresol green (BCG).

2. Theory

2.1. Spectrophotometry

The development of the present fibre optic probe is basically an extension of the spectrophotometric determination of pH. It makes use of at least one indicator dye, HI, to induce pH sensitive changes in absorption spectrum or colour. An indicator dye dissolved in a solution has the following relationship:

$$HI_{\substack{acidic \\ form}} \Leftrightarrow H^+ + I^-_{\substack{alkaline \\ form}} . \tag{1}$$
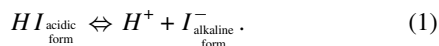
$[H^+]$, $[I^-]$ and $[HI]$ represent the various concentrations.

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

$$C = [HI] + [I^-]. \tag{2}$$

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

$$A(\lambda) = \alpha^I_\lambda [I^-]l + \alpha^{HI}_\lambda [HI]l \tag{3}$$

where α^I_λ is the molar absorption coefficient of the alkaline form and α^{HI}_λ is that of the acidic form of the dye and l is the absorption length. In the dye solution, the alkaline form of the dye peaks at a wavelength λ_1 which is 592 nm for BCP and 616 nm for BCG. The peak λ_2 corresponding to the acidic form is at 425 nm for BCP and at 420 nm for BCG. It is observed that increasing the pH reduces the absorbance peak at λ_2 and increases the peak at λ_1 (not shown).

2.2. Evanescent wave spectroscopy

Although electromagnetic radiation that strikes the core–cladding interface of a multi-mode optical fibre (OF) at angles greater than the critical angle is totally internally reflected, there is an electromagnetic field, called the evanescent wave (EW), that penetrates a small distance into the cladding. This EW, which decays exponentially from the core–cladding interface and propagating parallel to it, can interact with the species surrounding the core region where the cladding has been stripped off. If this EW is absorbed by the species surrounding the core region it gives rise to the phenomenon of attenuated total reflection and so the output power of the OF will be correspondingly decreased. The theoretical model of EW absorption spectroscopy using multi-mode fibres has been developed by Ruddy *et al* [13]. The power transmission in an OF, having a lossy cladding, is given by the modified Beer–Lambert's law:

$$P(l) = P_0 \exp(-\gamma l) \tag{4}$$

where l is the length of the unclad portion of the fibre, P_0 is the power transmitted in the absence of an absorbing species and γ is the EW absorption coefficient. Since $\gamma = f\alpha$, the above equation can be rewritten as

$$P(l) = P_0 \exp(-f\alpha l) \tag{5}$$

where f is the fraction of the power transmitted through the cladding and α is the bulk absorption coefficient.
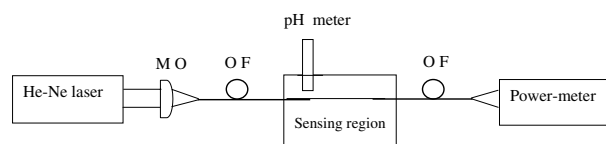

Figure 1. Experimental set-up: OF—optical fibre, MO—microscopic objective.

3. Experimental details

3.1. Probe fabrication

For fabricating the sensor probe a plastic clad silica (PCS) fibre with core diameter 200 μm and numerical aperture (NA) 0.22 is used. The total length of the fibre taken is 35 cm, of which 5 cm in the middle portion is unclad. Tetraethyl ortho silicate (TEOS) is used as the precursor for sol preparation since the refractive index of the porous silica film produced is less than that of the fibre core. BCP and BCG are used as the pH indicators. TEOS, anhydrous ethanol, water, HCl and the indicator dye are mixed in the molar ratio $1 : 4 : 1 : 0.02 : 10^{-4}$ at room temperature with the help of a magnetic stirrer. Ethanol acts as a common solvent for TEOS and water and HCl is used as a catalyst. The porous silica is coated on the unclad portion of the fibre using the dip coating technique with a PC controlled stepper motor. In this technique, the dipped fibre is pulled upwards at an optimized rate of 100 mm min^{-1}. An interferometric technique is employed to determine the thickness of the thin film and it has been found to be ∼200 nm for a single layer. The second layer is coated over the first one only after the complete curing of the latter and the third layer is coated in the same fashion. As a result, there exists an interface between the different layers. After drying the fibres at room temperature and atmospheric pressure, successive layers of dye-doped sol–gel thin films are coated onto the sensing region. These fibres are then kept for 15 days in order for the dye to become stabilized in the gel matrix and this reduces leaching of the dye molecules [12]. It is then washed in water to remove the excess and unbound dye. The coated region is again dried at 50 °C.

3.2. The experimental set-up

A 50 W tungsten halogen lamp with a monochromator (McPherson UV 275) and PMT (Oriel) are used to record the EW absorption spectrum of the FOS [14]. The experimental set-up used to calibrate the pH sensor is shown in figure 1. The laser emission at 633 nm of a He–Ne laser is coupled to the OF using a microscopic objective (MO) having almost the same NA as that of the fibre. Light intensity at the output of the fibre is measured using a power meter (Metrologic 45–545) and simultaneously the pH of the solution is monitored by a pH electrode (pH scan 2, MERCK), which has a sensitivity of 0.1 units. The pH value of the solution is varied by adding either HCl or NaOH.

4. Results and discussion

Figure 2 shows the normalized EW absorption spectrum of the pH sensor using immobilized BCP dye for different pH
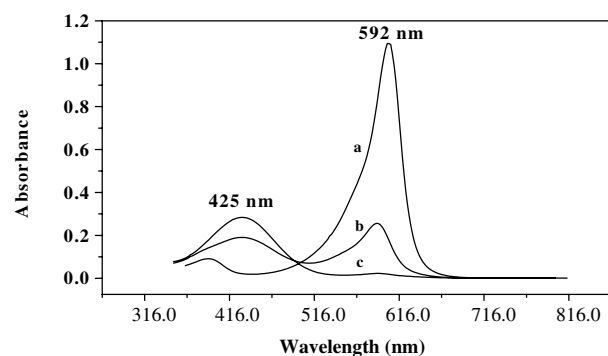
Figure 2. EW absorption spectrum of pH sensor with BCP in different pH environments ($a = 11$, $b = 8$, $c = 5$).
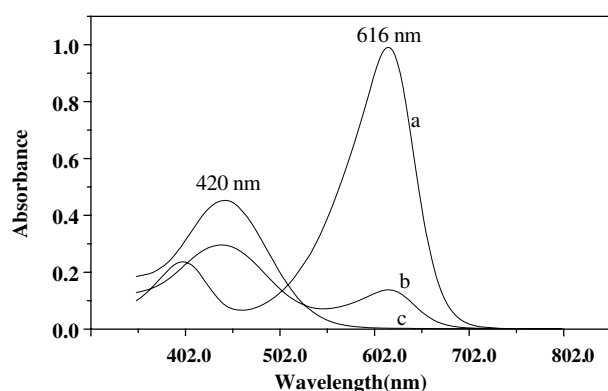

Figure 3. EW absorption spectrum of pH sensor with BCG in different pH environments ($a = 11$, $b = 8$, $c = 5$).

Figure 4. Sensor response with a single layer of BCP doped sol–gel thin film.

solutions surrounding the sensing region. The normalization is achieved by using the absorption spectrum of a fibre coated with an undoped sol–gel thin film. The EW absorption spectrum of the sensor is found to match well with that of a thin film of the dye coated on a glass substrate, which is obtained by using a spectrophotometer (Jasco V-570) which is not shown. As the pH of the solution surrounding the fibre increases, the absorbance of the alkaline form of the indicator increases and that of the acidic form decreases, but with smaller relative change. A similar type of plot is obtained for BCG dye as well (figure 3). So the wavelength of the light used to characterize the fibre optic pH sensor is to be near the absorption peak of the alkaline form of the indicator dye. This is the motivation for using a He–Ne laser as the source in this paper. Some of the properties of the sol–gel immobilized indicator dye differ from those in solution, which is in accordance with the observation made by Gupta and Sharma [12]. The pK value of BCP in solution is 6 and that in sol–gel matrix is 9 whereas for BCG it is 4.4 and 8, respectively. The pH range of BCP in solution is 5.2–6.8 and in sol–gel it is 7.5–10.5. BCG has a pH range of 3.6–5.2 in solution and 6.5–9.5 in sol–gel matrix.

Single layer coatings of BCP doped sol–gel thin film in the unclad portion of the OF gives only a poor sensitivity for the FOS, as can be inferred from figure 4. A similar kind of device performance has been observed for BCG also, which is not shown. This is evidently due to insufficient film thickness acting as the lossy cladding, which is only ∼200 nm. The penetration depth of the EW is of the order of the wavelength
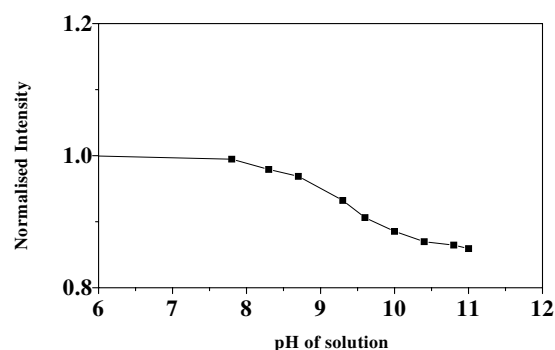
of light used, i.e. about 600 nm, which is much greater than a single layer thickness. So the EW entering the sensing region penetrates it and escapes into the surrounding medium (solution). Therefore, with insufficient thin film thickness the sensing region as well as the solution acts as the cladding. But only the portion of the EW in the sensing region will modify the output intensity. Hence the modified Beer–Lambert law cannot be applied here in the strictest sense.

Even though increasing the withdrawal rate can increase the thickness of the thin film, it is found that thicker films are found to crack during the sintering process due to high mechanical stress induced by the large shrinkage of the densifying film. These cracks cause a decrease in the effective coupling of the evanescent field, which reduces the sensitivity of the device in addition to increased scattering losses. Therefore we have adopted a new method to increase the thickness of the cladding (thin film) by using multiple sol–gel coatings. The existence of interfaces between different layers suppresses cracking of the film. So thick films produced by multiple sol–gel coatings are observed to be less prone to cracking. This procedure has been found to enhance the sensitivity of the device fabricated with BCP to a great extent (an increase of ∼70% fractional change in intensity). The plots in figure 5 illustrate the above-mentioned improvement in the device performance, which is fabricated. It is observed that a similar kind of behaviour is obtained with the pH sensor fabricated using BCG dye also as shown in figure 6. Two as well as three layers of dye doped sol–gel thin films have been coated on the unclad portion of the fibre to provide a systematic study of the effect of multiple sol–gel coatings.

Figure 7 shows that the EW absorbance of the thin film increases with increase in the number of layers. The EW absorbance is the product of EW absorption coefficient γ and the length of the sensing region L. Since the latter is a constant when the sensing length is fixed, the parameter which can account for the observed effect is γ, the product of bulk absorption coefficient α and effective fractional power f_e, through the sensing region. But α is a constant for a particular dye. Therefore the only parameter that can be varied to get a better sensitivity is f_e. This can be achieved by increasing the thickness of the sensing region. When the sensing region thickness is less than the penetration depth d_p as in the case with a single layer thin film coating, f_e is less than the actual fractional power f, which is the sum of the power transmitted through the sensing region and the power outside it, i.e. through the solution. So the effective fractional
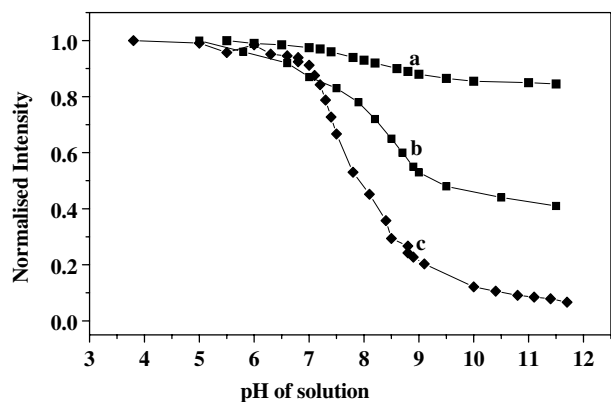
Figure 5. Response of the sensor fabricated with different layers of thin film containing BCP (a = 1 layer, b = 2 layers, c = 3 layers).
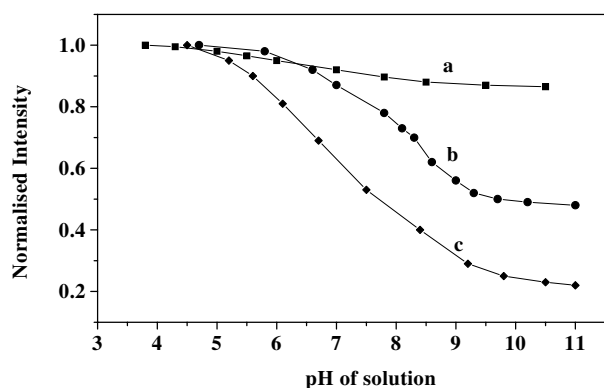

Figure 6. Response of the sensor fabricated with different layers of thin film containing BCG (a = 1 layer, b = 2 layers, c = 3 layers).
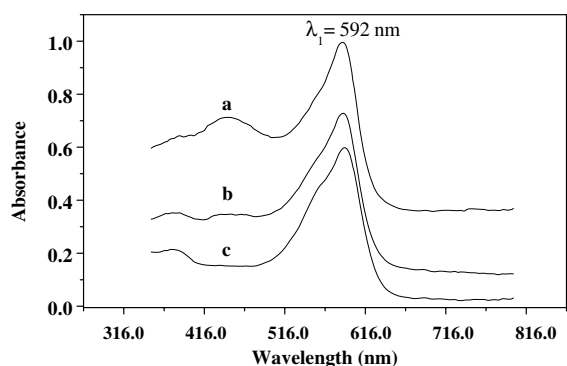

Figure 7. EW absorption spectrum of pH sensor with BCP in pH 10 with different thin film layers (a = 3 layers, b = 2 layers, c = 1 layer).

Figure 8. EW absorption spectrum of pH sensor with BCG in pH 10 with different thin film layers (a = 3 layers, b = 2 layers, c = 1 layer).

The improved sensitivity also indicates that there is a high level of interconnectivity between pores in different layers of the sol–gel thin film. The analyte (H^+ and OH^- ions) diffuses through the pores of the outer layer of the pH sensor and interacts with the indicator molecules present there. It then enters the inner layer and traverses through it and enters further into the next inner layer. Hence the dye in the innermost layer is also brought into interaction with the analyte. It can be assumed that the analyte molecules entering the outermost layer do not encounter the barrier between different layers of thin film and hence can react with the sensing species effectively, even near the core. Since the fraction of EW power is maximum in the innermost layer, the interconnectivity between pores has a significant role in the increased sensitivity of the present multi-layer fibre optic pH sensor.

The sensitivity of the device is found to be unaffected even after keeping it in low pH (acidic regime) environments for several days. But when the sensor is kept in alkaline solution for a long time the sensitivity is found to be decreased. This reduction in intensity is due to the leaching of the dye molecules from the gel matrix. The important factors that determine the leaching of a dopant from sol–gel derived films include the size of the dopant, the pore diameter of the sol–gel material and the solubility of the dopant in the solution. Since the first two factors are constants for a thin film when fabricated the only factor that may depend on the pH of the surrounding solution is the solubility of the dye in different pH environments. Similar results were observed by Butler *et al* [14] for another pH indicator dye, bromophenol blue, in a sol–gel matrix. From this it can be inferred that the leaching of the dye is significant at higher pH. The solubility dependence of BCP and BCG on pH value of the solution is the key factor. At very high pH increased leaching would be expected from sol–gel silica films due to alkaline attack, which results in dissolution of silica. This also contributes to the observed effect of decrease in sensitivity at very high pH environments. The sensor is found to give similar results even after storage for a period of three months.

The response time of each type of sensor (with single layer, double layer, etc) is found to depend on the direction in which the pH of the solution is varied. The temporal response of a sensor with BCP is shown in figure 9. An unclad fibre dipped in dye solution shows almost equal response times in both directions of pH variation. For the sensor fabricated with a

power in the sensing region, which is available for intensity modulation at the fibre output, increases with increase in the number of thin film layers. The optimum thickness of the thin film is nearly equal to the penetration depth of the EW. When the film thickness becomes greater than the penetration depth, the temporal response of the sensor may be adversely affected as the analyte has to traverse a longer distance through the gel matrix. The EW absorption spectra of BCG show that absorbance of the sol–gel thin film increases with increase in the number of layers, as shown in figure 8 which is similar to the results obtained for BCP.
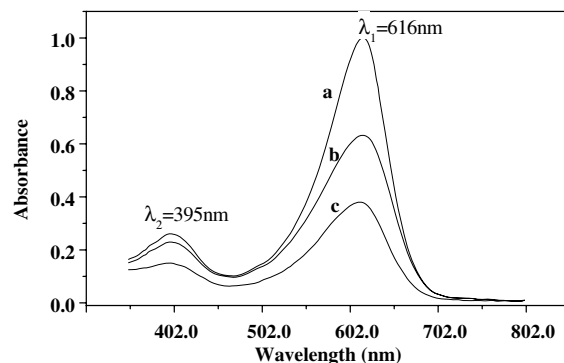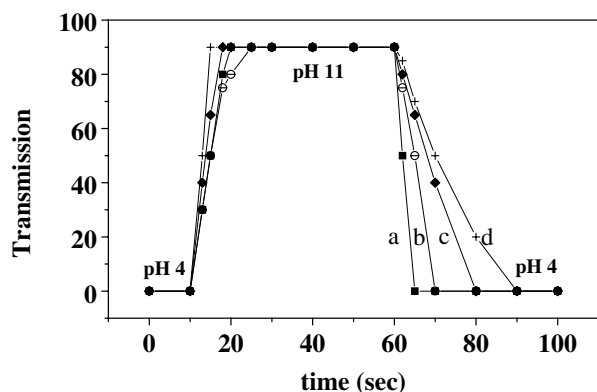
Figure 9. The temporal response of the fibre optic pH sensor with BCP ($a = 1$ layer, $b = 2$ layer, $c = 3$ layer, $d = 4$ layer).

single sol–gel layer the response time for a low to high pH variation is almost the same as that for a high to low variation. From figure 9 it is obvious that, as the number of layers is increased, the response time increases. A low to high pH variation shows a response time of 5 s and a slow response time of about 30 s is observed in the reverse case for a sensor produced with a three-layer sol–gel thin film coating. A similar graph is also obtained for BCG (not shown).

5. Conclusion

The fabrication and characterization of a EW FOS is discussed. This work is carried out by immobilizing a pH sensitive dye (BCP as well as BCG) on the unclad portion of the optic fibre. This procedure gives a fractional change in intensity of only 15%, leading to poor sensitivity of the device. The thickness of the thin film has been found to be ∼200 nm, which is much less than the EW penetration depth. Multi-layer sol–gel coating impregnated with dye has been found to increase the sensitivity considerably. It can be inferred that there is a high level of interconnectivity between pores in different layers of dye doped sol–gel thin films. This also contributes to the increased sensitivity of multi-layer sol–gel coatings. However, the response time of the sensor has been found to be adversely affected by increasing the number of layers. The pH value of the fluid can be monitored continuously without a break, unlike a pH electrode. The operating range of the sensor can be increased by mixing various dyes in the earlier stages of sol preparation as done by Gupta and Sharma [15]. Even though high sensitivity of this FOS prevents its use as a long-range pH sensor with more than one pH indicator dye, such sensors can be built by carefully adjusting the sensitivity with multiple coatings and with varying sensing lengths.

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