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

S Thomas Lee¹, Jose Gin², V P N Nampoori¹, C P G Vallabhan¹, N V Unnikrishnan² and P Radhakrishnan¹

¹ International School of Photonics, Cochin University of Science and Technology, Cochin-682 022, India
² School of Pure and Applied Physics, Mahatma Gandhi University, Priyadarsini Hills PO-686 560, India
E-mail: lee@cusat.ac.in and radhak@cusat.ac.in

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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:

\[ H^+_{\text{acidic form}} + C_{\text{alkali form}} \rightleftharpoons H^+_{\text{alkali form}} + C_{\text{acidic form}} \]

(1)

\[ [H^+]_{\text{acidic}} \], \[ [I^-] \] 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

\[ C = [HI] + [I^-]. \]

(2)

The absorbance \( A \) of the solution, which is a function of the wavelength \( \lambda \), is related to \( [HI] \) and \( [I^-] \):

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

(3)

where \( \alpha_I \) is the molar absorption coefficient of the alkaline form and \( \alpha_{HI} \) 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 \( \lambda_1 \) which is 592 nm for BCP and 616 nm for BCG. The peak \( \lambda_2 \) 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 \( \lambda_2 \) and increases the peak at \( \lambda_1 \) (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:

\[ P(l) = P_0 \exp(-\gamma l) \]

(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 \( \gamma \) is the EW absorption coefficient. Since \( \gamma = f \alpha \), the above equation can be rewritten as

\[ P(l) = P_0 \exp(-f \alpha l) \]

(5)

where \( f \) is the fraction of the power transmitted through the cladding and \( \alpha \) is the bulk absorption coefficient.

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 : 0.2 : 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 1. Experimental set-up: OF—optical fibre, MO—microscopic objective.](image-url)
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 $\gamma$ 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 $\gamma$, the product of bulk absorption coefficient $\alpha$ and effective fractional power $f_e$, through the sensing region. But $\alpha$ 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
The results obtained for BCP.

absorbance of the sol

gel matrix. The EW absorption spectra of BCG show that
affected as the analyte has to traverse a longer distance through
depth, the temporal response of the sensor may be adversely
When the

number of thin

modulation at the

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
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.

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

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).

358
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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