Available online at www.sciencedirect.com
ScienceDirect
Sensors and Actuators B 129 (2008) 94–98
SENSORS AND ACTUATORS B CHEMICAL
www.elsevier.com/locate/snb

Broad range pH sensor based on sol–gel entrapped indicators on fibre optic

Saying Dong [a,b,*], Ming Luo [a,b], Gangding Peng [c], Wenhua Cheng [a,b]

[a] State Key Laboratory for Marine Corrosion and Protection, Qingdao, Shandong Province 266071, PR China
[b] Luoyang Ship Material Research Institute, Luoyang, 471039, PR China
[c] School of Electrical Engineering, University of New South Wales, Australia

Received 31 October 2006; received in revised form 7 June 2007; accepted 19 July 2007
Available online 25 July 2007

Abstract

A broad-range fibre optic pH sensor based on evanescent wave absorption is presented in this paper. This sensor is prepared by immobilizing a mixture of three pH sensitive indicators (dyes): cresol red, bromophenol blue and chlorophenol red onto the unclad fibre surface using a sol–gel cladding technology. Triton is introduced into the sol–gel cladding to improve the cladding quality. Smooth and strong sol–gel cladding with entrapped indicators and triton has been fabricated and observed using a scanning electron microscope (SEM), an energy dispersive X-ray detector (EDX) and an atomic force microscopy (AFM). The pH sensor based the cladding has shown a linear, reversible and repeatable response over a broad range of pH values between 4.5 and 13.0.

Keywords: pH sensor; Optical fibre sensor; Sol–gel; Indicator; Triton

1. Introduction

The measurement and control of pH is widely required in chemical, biomedical, environmental science and engineering in addition to industrial applications. For example, the detection of the pH value below 10 can indicate potential corrosion of reinforcing tensors in civil engineering structures which are on earth, underground or in underwater conditions [1]. Hence, there is continued interest in developing new techniques for pH detection [2,3]. 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 fibre optic pH sensors [4–6]. This is because fibre optic sensors offer many advantages such as small size, immunity to electromagnetic and radio frequency interference, and multiplexing capability.

Optical fibre pH sensors are based on pH-induced reversible changes in optical or spectroscopic properties such as absorbance, reflectance, fluorescence, energy transfer, refractive index [7,8], etc. Its key part is a pH sensitive cladding or film. It can be prepared by immobilizing a pH sensitive dye into a polymer matrix, or by covalent linking of an organic dye onto the tip or sides of an optical fibre. In previous reported work, pH sensitive dyes, which are usually weak organic acid with absorption over the visible range, are used as optical transducers.

The immobilization process can be performed using different methods [9,10]. The most popular one is the sol–gel method where a porous silica matrix is formed while entrapping the dye molecules within it. Porosity of the matrix enables penetration of the analyses and protons, and allows their easy access to the dye molecules which are permanently anchored. The sol–gel method is quite simple. Apart from its simplicity, the film produced by the sol–gel technique is tough, inert, and more resistant to aggressive environments than those by other techniques [11,12].

Despite their favorable characteristics, optical fibre pH sensors are inherently limited by their narrow pH range. This is because these sensors do not measure pH values directly. Instead, they usually measure the concentration of an indicator or dye in

* Corresponding author at: State Key Laboratory for Marine Corrosion and Protection, Qingdao, Shandong Province 266071, PR China.
Tel.: +86 53285843208; fax: +86 53285826553.
E-mail address: dongsaying@sina.com (S. Dong).

0925-4005/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.snb.2007.07.078

its acid or base form. Therefore, the measurement depends on the pK_a of the dye and the pH range is typically restricted to about 3–4 pH units. Here K_a is a dissociation constant of the dye, so the development of sensors for an extended pH range is desirable. In this regard, it has been proposed and demonstrated that the measurable pH range can be extended by using indicators with two or three pK_a values, several indicators together or a group of similar dyes with different pK_a values [13,14].

In this paper, we also used several indicators together to extend the pH range. Gupta and Sharma [14] adopted the indicators of cresol red, bromophenol blue and chlorophenol red and described the measuring range of each indicator. However, as a variant from previous work, we added a surface active reagent, triton, together with the three pH sensitive dyes to prepare the dye-entrapped sol–gel cladding on the surface of the unclad fibre. We found that the introduction of triton improved the quality of the sol–gel cladding and the cladding worked well over a broad dynamic range of 8–9 pH unit.

2. Experimental

2.1. Chemical reagents and materials

Tetraethylorthosilicate (TEOS) and chlorophenol red were obtained from Aldrich Chemical Co. (Fluka Company). The following chemicals were purchased from Qingdao chemical reagent company: cresol red, bromophenol blue, anhydrous ethanol, benzene, nitric acid, hydrochloric acid and sodium hydroxide. 0.1 mol/L Hydrochloric acid (HCl) and 0.1 mol/L sodium hydroxide (NaOH) were used to adjust the pH to the desired value.

All the silicon reagents are sensitive to moisture and were stored under dry nitrogen gas. All other chemicals were used without any further purification. All aqueous solutions were prepared with deionized water and all chemicals were of analytical reagent grade.

2.2. Preparation of sol–gel cladding

Fabricating the pH sensor involved removing the original fibre cladding and reducing the fibre diameter to about 60 μm by chemical etching using hydrofluoric acid (HF). The etched length of the fibres to be clad with the sol–gel cladding was about 4 cm. The unclad part of the fibre was washed with deionized water, then with the mixture of acetone and ethylene chloride (1:1, v/v).

After cleaning, the OH groups on the surface of the unclad fibre were activated by treating it into a 30% HNO_3 solution. These OH groups activated on the unclad fibre surface formed bonds with the silica molecules in the porous glass film and helped the thin film adhere to the surface. Tetraethyl ortho silicate (TEOS) was used as the liquid precursor for preparing the pure silica film on the unclad fibre because it gave a porous silica glass of refractive index less than that of the fibre core, thus allowing the wave guidance condition to be met. TEOS can form a three-dimensional network of silicon dioxide (SiO_2) through hydrolysis and condensation polymerization processes. The indicator dyes will be entrapped in the structure without leaching.

The solution was prepared at room temperature using 3 ml of TEOS, 3 ml of anhydrous ethanol, 1 ml deionized water mixed with 3% Triton X-100, along with 4.6 mg cresol red, 8.2 mg bromophenol blue and 4.2 mg chlorophenol red. Triton is a type of surface active reagent and can effectively reduce cracks on the sol–gel film.

After mixing, the solution was stirred for 60 min at 60 °C. Sol–gel cladding was performed by putting a drop of the silica sol on the unclad fibre and shifting it from one side to the other until a uniform sol–gel cladding was formed. After coating, the fibre was dried at atmospheric pressure and room temperature for 20 days. It was then immersed in water to allow the excess and unbound indicators to be removed.

2.3. Instruments

The fibres tested in our experiments were 62.5/125 multimode fibres produced by the Furukawa Electric Co. Ltd. Its NA is 0.2. The main material of the core and cladding was silicon dioxide, but a small quantity of germanium element was introduced into the core.

The micro appearances of sol–gel cladding with pH sensitive indicators were observed by an environment scanning electron microscope (ESEM, model XL30) from the Philips Corporation and atom force microscope (AFM) (SPI3800N) from NSKLTD in Japan. The energy spectrum analysis of the sol–gel cladding was also finished by the ESEM to discover the element contents in the cladding. Solution pH was measured with a pH meter from Shanghai Precision & Scientific Instrument Co. Ltd.

The optical measurement system for the characterization of the fibre-optic sensor is the same as described in our previous paper [15]. The experimental set-up for testing different pH conditions is shown in Fig. 1. The light source was FOD 2110 with a wavelength of 650 nm from Fibre Optic Devices, Ltd. (Russia). The coated portion of the fibre was held in the middle of the cell. A model 577L power meter from Rifocs Corporation

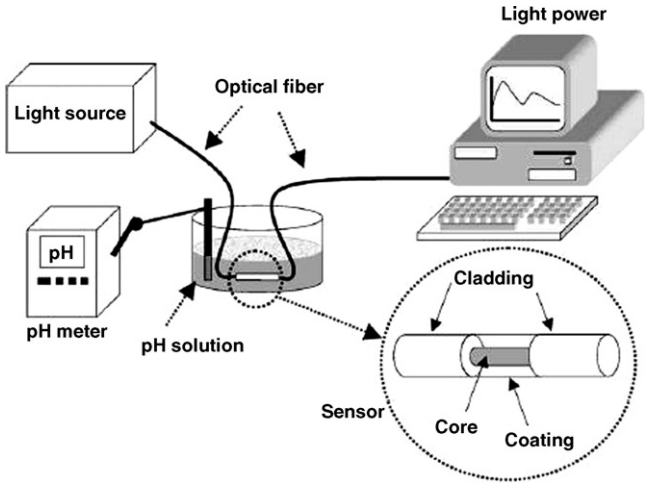

Fig. 1. Schematic diagram of the optical fibre pH sensor and its experimental set-up.