

Fiber Optic pH Sensor Development

M. Janowiak, H. Huang, S. Chang, and L. H. Garcia-Rubio*

University of South Florida, Tampa, FL, USA

Telephone: (813) 974-5854 Fax: (813) 974-3651

janowiak@eng.usf.edu, garcia@eng.usf.edu

*To whom correspondence should be addressed. On leave at Ocean Optics, Inc. 380 Main Street, Dunedin, FL. Phone: (727) 733-2447 Fax: (727) 733-3962.

LuisG@oceanoptics.com

Abstract

Fiber optic chemical sensor technology is a field of growing importance with diversified applications in oceanography, chemical process, clinical diagnosis, and environmental monitoring. The goal of this study is to develop the technology to support specific analytical reagents on polymeric membranes for fiber optic based pH sensors. For on-line process control applications, pH sensors must have a fast response, high sensitivity, and be able to withstand relatively high temperatures. To meet these requirements, a synthesis strategy resulting in a three-layered probe has been developed. The technique grows a hydrophilic polymer matrix from a fiber optic and incorporates specific pH indicator dyes. This paper reports on the synthesis conditions of the polymer matrix to attain light transparency, thermal and mechanical stability. The implications of the matrix behavior relative to the interpretation of the signal and to the flexibility of the system for its use with other indicators is also presented and discussed. For detection purposes the probes are configured in both transmission and reflectance modes. The reflectance configuration of the pH probe is ideal for on-line process monitoring of slurries since it is not affected by the problems of fouling or slurry concentration. A comprehensive mathematical model has been developed to obtain pH from the spectrophotometrically measured dye concentrations. This model accounts for pertinent physicochemical effects, such as temperature, ionic strength, and the buffering capacity of the polymer matrix-dye system. Optical effects such as scattering from the polymer matrix and wavelength corrections due to the difference in refractive index between the support matrix and the medium are also included in the model. It is demonstrated that precisions of the order of ± 0.001 pH units are attainable.

Introduction

pH is an important parameter for many applications in the medical field, environmental monitoring, and industrial processes. Fiber optic pH sensors are advantageous for on-line applications, since they are more durable than the standard electrodes and have a direct interface to computers aiding in control schemes. Some of the requirements for an optical pH sensor to be used on-line are fast response time, high sensitivity, and durability. These criteria are important for control applications, where a fast response time is essential. To meet these requirements, a three-layered support matrix has been developed, which incorporates the indicator dyes in the outer polymeric layer [1]. It has been demonstrated that the matrix is stable on the fiber surface after being soaked in water at high temperatures and pressures. The conditions for synthesis are discussed below. In order to obtain pH from the spectrophotometrically measured

dye concentrations a comprehensive interpretation model has been developed [2]. The model takes into account physicochemical effects on the membrane as well as optical corrections. The whole UV-vis range of interest for a particular indicator is used, providing redundancy for improved statistics and more accurate and precise measurements. With this system, precisions of ± 0.001 pH units are attainable. This sensor can be configured in either transmission or reflection mode. Using a reflection configuration, the sensor can be placed directly in slurry materials, since the membrane is not susceptible to fouling as the standard electrodes are. This design also lends itself to the monitoring of several chemical species, O₂ or metals, for example. Multiple indicators dyes could be used, or multiple fiber bundles. This paper reports on the synthesis conditions for the support matrix and the comprehensive interpretation model.

Synthesis

A three-layered support matrix has been developed that incorporates chemically sensitive indicator dyes in the outer layer, depicted in Figure 1. The strategy for synthesizing the matrix is presented next.

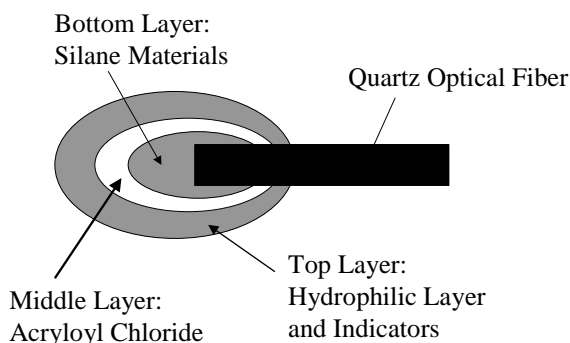


Figure 1. Three-layered design of the fiber optic pH sensor.

The surface silanization of the glass slide or fiber surface is a key step in attaching the matrix and insuring that it is stable on the surface [3]. The conditions for synthesis are as follows [1]. A 0.28 mmol/L aminopropyltriethoxysilane aqueous solution is prepared by mixing 1.3 ml 3-aminopropyltriethoxysilane with 20 ml deionized water in a small bottle with a cap, then adjusting it to pH=2 with HCl and heating to 75°C in an oven for 30 minutes. A glass slide, 1 x 3.6cm, is submerged in the solution and maintained at 75°C for 50 minutes. Then, the slide is removed from the bottle and dried at 165°C for 3 hours under an argon purge. The groups in the resulting layer were confirmed using IR spectroscopy. IR(KBr): 3500 cm⁻¹ (s), 3160 cm⁻¹(s), 1640 cm⁻¹(m), 1590 cm⁻¹(m), 1140 cm⁻¹ (s). In the synthesis, 3-aminopropyltriethoxysilane is cleaved using HCl to form free silanol groups and ethanol. This reaction is an equilibrium reaction forced to completion by keeping the temperature at 75°C evaporating the produced ethanol. The HCl was used to protect the amino groups and prevent them from participating in the reaction. The silanol groups deposit on the glass surface, in a condensation reaction. This is a favorable reaction due to the similarity in structure of the silanol groups and glass. The viscosity of the solution suggests that the silanol groups are also condensing on themselves forming oligomers. The polymerization is kept from

going to completion by the water in the solution. The reaction is run for 2.5 to 3.5 hours at 165°C.

An important factor in insuring this layer is stable on the glass surface is the number of hydroxyl groups remaining after the condensation reaction. The more hydroxyl groups, which are hydrophilic, the more likely the layer is to peel off the glass surface when submerged in water at high temperatures. The concentration of 3-aminopropyltriethoxysilane can be optimized to obtain the minimum remaining hydroxyl groups, and was determined to be 6.5% by volume. With these conditions, this layer is about 3 to 4µm thick.

The second layer is used to bridge the silica chemistry of the first layer and the carbon chemistry of the outer layer. Next the slide is treated with pyridine for 4 hours to remove any HCl. The first layer is then reacted with acryloyl chloride at room temperature for 3 hours to incorporate the vinyl groups. The reaction is conducted in the dark to protect the double bonds from reacting. The IR spectra yielded peaks at the following locations, 3500 cm⁻¹(s), 3160 cm⁻¹(s), 1720 cm⁻¹(m), 1640 cm⁻¹(m), 1590 cm⁻¹(m), 1140 cm⁻¹(s). The peaks at 1720cm⁻¹ and 1640cm⁻¹ are characteristic of carbonyls and carbon-carbon double bonds, respectively.

The third layer is grown from the double bonds incorporated in the middle layer. The polymerization is as follows. A beaker containing a mixture of 2.1745 g (0.3 mol) of acrylamide, 0.3658g (0.0024 mol) of N,N-methylene bisacrylamide, 0.5 ml (0.0046 mol) of 4-vinylpyridine, 0.9703 g (0.004 mol) of ammonium persulfate, 20 ml of ethanol and 20 ml of deionized water is stirred on a hot plate magnetic stirrer. An activated glass slide is put in the beaker, which is sealed with Parafilm and heated to a reaction temperature of 78°C for 20 minutes, after which a polymeric gel is obtained. The ratio of N,N-methylene bisacrylamide to acrylamide can be varied to give different degrees of crosslinking. This will effect the stability of the matrix and the response time. The higher the degree of crosslinking the more stable the matrix will be but the slower the response time. The optimization of the third layer is under investigation. Ammonium persulfate is used as the initiator for the solution polymerization, because it does not absorb in the UV-visible region. This will give a wide spectral window to detect different indicator dyes. Phenol red for example can be used for solutions having a pH from 4 to 12 and has peaks at about 430nm and 560nm. Pyridine, which is a good indicator for low pH solutions, absorbs in the UV region with a peak around 255nm. For polymerization on fibers, using a photochemical initiator is ideal. By controlling the intensity and duration of the light, the thickness of the polymer layer can be tightly controlled. One of the challenges of photopolymerization is choosing an initiator that is transparent in the UV-vis region. Most photo-initiators have an aromatic ring that absorbs in the UV region. The optimization of the photopolymerization is still under investigation. The indicator used in these studies is pyridine. As mentioned this indicator is good for low pH solutions. It is a vinyl indicator and is polymerized in the third layer, ensuring that there is no leaching of the dye. A wide variety of indicators can be entrapped or polymerized in this layer. Tyrosine, which is a biocompatible indicator, could be used for medical applications, for example. This design also lends itself to the use of multiple indicators or multiple fiber bundles.

This method yields a transparent three-layered support matrix from 250nm to 800nm. The matrix has been tested for stability on the glass surface. It does not peel off

the surface after being soaked in water for eight months or after being autoclaved at 120°C. Stability is maintained when dried in an oven as well.

Interpretation of the Spectral Signal

A mathematical model has been developed to obtain pH from the spectrophotometrically measured indicator dye concentrations [2]. The Henderson-Hasselback equation is used to relate the concentrations of the protonated and dissociated forms of the dye to pH. Using Beer-Lambert law, the concentration of each species can be related to the spectral signal.

$$pH = pK_a + \log \frac{[A^-]}{[HA]}$$

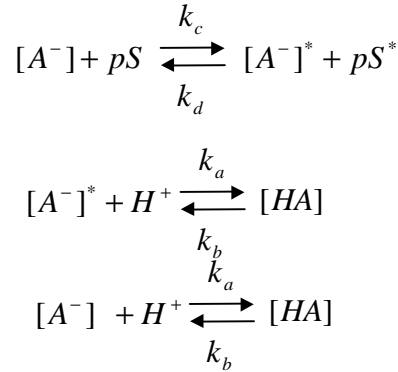
$$\tau(\lambda) = \lambda \sum_{i=1}^N C_i \varepsilon_i(\lambda)$$

where $[A^-]$ and $[HA]$ are the concentrations of the dissociated and protonated forms of the indicator, $i = 1, 2$, respectively. τ is the optical density as a function of wavelength. The model also accounts for physicochemical effects on the membrane such as ionic strength, temperature, and buffering capacity of the indicator dye. The optical effects from the swelling and scattering of the membrane are addressed as well. The comprehensive interpretation model is as follows [2],

$$pH = pk_{ao} + P \log(Cond) + M \left(\frac{1}{T} \right) + \log \frac{[A^-]}{[HA]}$$

where $Cond$ is the conductivity of the solution, T is the temperature, and P and M are calibration parameters.

The ionic strength of the solution affects the calculated pH through the equilibrium constant of the indicator dye. It has been shown that at low ionic strength the pk_a of the indicator is no longer constant [3]. The locally high concentration of dye yields charged groups in the polymer matrix. At low ionic strength, hydrogen ions neutralize the negative charges in the membrane causing a buffering effect. This results in a shift in the equilibrium constant. As the concentration of positive ions increases the negative charges are shielded lessening the buffering effect and the affect on the equilibrium constant. Since the buffering effect causes a shift in the equilibrium constant it is necessary to know the dye concentration in order to compensate for this effect. The dye concentration should be optimized to minimize the buffering effect while maximizing the signal-to-noise ratio of the sensor. The following kinetic model has been proposed to account for the effects of ionic strength [2].



The salt, S , collides at frequency p with reactant $[A^-]$ bringing both to excited states, S^* and $[A^-]^*$. Both the excited analyte $[A^-]^*$ and the unexcited analyte $[A^-]$ react with the hydrogen ions at different rates. This mechanism essentially proposes two different rates of reaction depending on the interaction of the analyte with the salt in the solution. $[S/S^*]$ is directly proportional to the ionic strength, $[S/S^*] = -k'[I]$. Combining the equilibrium constants and incorporating the relation for ionic strength, the following is obtained $K_a = \frac{[A^-][H^+][I]^p}{[HA]}$. Taking the logarithm, the equation becomes

$$pK_a = pH - \log \frac{[A^-]}{[HA]} - p \log I.$$

In terms of the thermodynamic equilibrium constant,

$pK_a = pK_{a0} + P \log I$, where $P = -p$. This correction to the equilibrium constant adequately represents the behavior of several indicator dyes. A more convenient measurement than ionic strength to take is conductivity. The two are related as follows,

$I = \frac{1}{2} \sum_i C_i Z_i^2$ and $Cond = F \sum_i |Z_i| u_i C_i$, where C is the concentration of ions, Z is the charge, F is Faraday's constant, and u is the mobility. The mobility is defined as $u_i = \frac{|Z_i|e}{6\pi\eta r_i}$, where e is the charge of one electron, η is the viscosity of the medium, and r is the radius. Equating the two and taking the logarithm, in terms of conductivity $\log I$ is replaced by $-\log \frac{Fe}{3\pi\eta r_i} + \log Cond$.

The temperature is another factor on the dissociation constant. This dependence was represented by an Arrhenius relationship, $k(T) = A \exp \frac{-E}{RT}$, where A is the pre-exponential factor, E is the activation energy, R the gas constant, and T temperature. In terms of the equilibrium constant, $K_a = \frac{k_1}{k_2} = \frac{A_1}{A_2} \exp \frac{(E_2 - E_1)}{RT}$, where k_1 and k_2 are the rate constants of the forward and reverse reactions in the indicator dye reaction. Taking the logarithm and combining terms the equation takes the form, $pK_a = A' + M \frac{1}{T}$. A' is

related to the log of the ratio of the pre-exponential factors, and M is related to the difference in the activation energy of the forward and reverse reactions.

The combined expression accounting for the effects of ionic strength and temperature on the equilibrium constant is the following [2],

$$pK_a = pK_{ao} + P \log(Cond) + M \left(\frac{1}{T} \right)$$

where pK_{ao} , P , and M are calibration parameters.

Along with the physicochemical effects on the measurement, there are also biases due to the swelling and scattering of the membrane. The refractive index difference between the solution and the membrane causes a shift in the spectrum. This shift can be corrected by relating the wavelengths in the two different mediums to a reference such as the wavelength in vacuum, λ_o . The wavelength in medium 1 is displaced by the ratio of

the refractive index times the wavelength in medium 2, $\lambda_1 = \lambda_2 \frac{n_2}{n_1}$, where n_1 and n_2 represent the refractive index of medium 1 and 2 respectively.

Another necessary optical correction is required to compensate for the scattering due to the polymer matrix. Although the polymer is chosen to be transparent in the range of absorption of the indicator dyes, it may still scatter light significantly. There are rigorous solutions for scattering available, such as the Rayleigh approximation for small non-absorbing scatterers. The scatterer dimensions must be a twentieth of the wavelength and the ratio of the refractive index of the scatterers relative to the suspending medium not much larger than unity. Since the polymers are chosen to be non-absorbing and the swelling of the matrix keeps the refractive index ratio close to one, a simple semi-empirical model based on the Rayleigh approximation [4], $\tau(\lambda) = k\lambda^{-s}$, can be used to compensate for the membrane scattering.

The scattering correction along with the corrections for the physicochemical effects on the measurement are used in an optimization routine developed in house to solve for the dye concentration. With this system, precisions on the order of ± 0.001 pH units are attainable.

Conclusions

A three-layered support matrix has been developed incorporating chemically sensitive indicator dyes in the outer polymeric layer. The similar chemistry of the inner layer to that of glass ensures that the membrane will not peel off the fiber surface. In order to obtain pH from the spectrophotometrically measured dye concentrations, a comprehensive mathematical model has been developed. This model accounts for pertinent physicochemical effects due to the membrane, such as ionic strength, temperature, and the buffering capacity of the dye. Additional corrections required by the scattering of the polymer matrix and by differences in refractive index of the solution and membrane are made. With this system, precisions on the order of ± 0.001 pH units are attainable. In either the transmission or reflectance configuration, this sensor is well suited for many environmental, industrial, or medical applications.

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