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Construction and evaluation of an optical pH sensor based on polyaniline–porous Vycor glass nanocomposite

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Abstract

This work describes the preparation of a polyaniline (Pani)–porous Vycor glass (PVG) nanocomposite and its use as sensing phase in an optical fibre pH sensor. Nanocomposites of Pani–PVG were prepared by in situ polymerisation of aniline absorbed inside the pores of a PVG (Corning 7930) with an average porous size of 8 nm. The optical sensor was constructed by fixing a PVG slide onto a distal end of bifurcated optical fibre bundle, with a cyanoacrylic resin. The sensor response was found to be reversible in the pH range from 5 to 12 and linear from pH 7.4 to 9.5. Response times of 4, 8 and >16 min were obtained for slide thickness' of 0.5, 1 and 1.5 mm, respectively. Changes of temperature, ranging from 20 to 40°C, showed minor effect on the dynamic range. Similarly, the ionic strength (0.15, 0.30 and 0.50 mol l^{-1}) and the nature of the ions (NaCl, KCl and $NaClO_4$) showed minor influence on the sensor response. Leaching of Pani was not observed and the sensor lifetime was determined as being at least 5 months. These results indicate that a Pani–PVG nanocomposite is suitable for the construction of optical pH sensors, with good analytical performance, since the glass slides can be prepared with good reproducibility and durability. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Polyaniline; pH optodes; Nanocomposites; Porous Vycor glass

1. Introduction

Optodes for pH determination have been frequently described in the literature [1–3]. They are usually based on acid–base indicators, which can be adsorbed on the surface of support matrices [4,5], chemically immobilised in an appropriate support [6–9] and physically entrapped in a polymeric matrix [10]. As the sensing species are weak acids whose protonated and non-protonated forms show different spectral properties, these types of optodes present sigmoidal response curves and responses dependent on the ionic strength of the solution. Despite the sigmoidal response showed by these sensors, a narrow range of the curve can be usually taken as linear (ca. 2 pH units), in order to simplify the calculation of sample pH by interpolation method. In addition, the indicator can be prone to leaching, mainly when it is not covalently immobilised to the support matrix, which therefore, can affect the sensor lifetime.

Attempts have been made in order to extend the pH response range of optodes, by employing, for example, fluorescent indicators [8], indicators with two acid groups [11] or two indicators with different acidic constants [12]. Studies have also been carried out to verify the influence of the ionic strength on analytical signal as function of the properties of the support matrix [13]. A methodology for determination of ionic strength of solutions, based on these effects, has been even proposed [13].

Polyaniline (Pani), due to its interesting characteristics, has attracted attention of researchers of different fields, such as chemistry and physics [14,15]. Besides being easily synthesised, this polymer shows high electric conductivity, high stability [16,17], and undergoes a colour change when submitted to a variation of pH [18] or electrical potential [19]. In fact, Pani, as well other conducting polymers, can be considered as a polyelectrolyte with several pK_a values, offering the possibility of construction of optodes with wider dynamic range [20,21].

Although, these properties make Pani (and its derivatives) an advantageous polymer for the construction of chemical sensors [20,22], it shows low solubility in common organic solvents, which causes difficulty in the preparation of films,

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restricting, therefore, its use. In order to overcome this drawback, many studies have been made to produce a more soluble polymer (or its derivatives), maintaining the usual characteristics such as mechanical resistance, stability and chemical behaviour [23–27]. Li et al. [23] have described the synthesis of polyanilines which are soluble in common organic solvents, such as DMF and DMSO, by using organic proton acids of large molecular size (*p*-toluenesulphonic acid or sulphanilic acid) or graft polymerisation with polyaminostyrene. Macinnes and Funt [24] have used *o*-methoxyaniline to produce polymethoxyaniline, which is soluble in DMF, acetonitrile and trifluoroacetic acid. Low temperature polymerisation of aniline using ammonium peroxodisulphate have been used by Abe et al. [25] to synthesise high molecular weight Pani which is soluble in *N*-methyl-2-pyrrolidone. The polymerisation of aniline in acetonitrile by employing copper(II) perchlorate as oxidant agent, as described by Inoue et al. [26], yields Pani perchlorate that is soluble in DMSO, ethanol and chloroform. Bergeron et al. [27] have described the water-soluble poly(aniline propane sulphonic acid), prepared by derivatisation of Pani.

Besides these efforts to produce a more soluble Pani, which can allow the preparation of films with improved characteristics, attempts have also been made in order to obtain immobilised Pani from the monomer in a single step. As far as optical sensors are concerned, Ge et al. [28] have constructed an optical pH sensor based on evanescent waves, by immobilising Pani directly onto the core of a silica optical fibre. Pringsheim et al. [29] have prepared Pani films directly on the surface of a polystyrene cuvette, by polymerising the monomer in acidic medium employing ammonium peroxodisulphate as oxidant agent. The film thickness was controlled by discharging the solution and washing the cuvette several times with distilled water.

Zarbin et al. [30,31] have described the acidic chemical polymerisation of aniline in the porous cavities of Vycor glass (PVG (Corning 7930)), producing the Pani–PVG nanocomposite. The very narrow pore size distribution of the glass prevents the occurrence of intermolecular interactions, structural defects and cross-linking, providing the formation of molecularly isolated polymeric chains. Therefore, this nanocomposite can be produced with high reproducibility, without modifying the chemical properties of Pani. The reversible colour change of Pani–PVG composite from dark green (emeraldine salt) to dark blue (emeraldine base) when the glass is immersed in acidic solution and basic solution [31,32], respectively, indicates the usefulness of this material as sensing phase for optical pH sensor.

This work describes the preparation of a Pani–PVG nanocomposite and its use as a sensing phase in an optical fibre pH sensor. The sensor was evaluated with respect to dynamic range, response time, reproducibility, durability and effects of temperature and ionic strength of the solution on the analytical signal.

2. Experimental

2.1. Reagents and solutions

All reagents used in this work were of analytical grade. Aniline was vacuum distilled before use. Buffer solutions in the pH range from 4 to 12 were prepared as recommended [33], by employing 0.05 mol l^{-1} boric acid, 0.20 mol l^{-1} citric acid and 0.10 mol l^{-1} trisodium *o*-phosphate. The ionic strength of the buffer solutions were varied by adding 0.15, 0.30 or 0.50 mol l^{-1} of NaCl, KCl or $NaClO_4$ when convenient. The pH of every buffer solutions were checked by employing a pH electrode, connected to a pH meter (±0.01 pH unit).

2.2. Preparation of the nanocomposite and construction of the pH optode

A PVG (Corning 7930) with an average porous size of 8 nm and superficial area of 166 $m^2 g^{-1}$ [34] was employed for the construction of the sensor. Glass slides (10 mm ×10 mm and ca. 1.5 mm thick) were cut from a PVG plate and carefully sanded to adjust their thickness' to 0.5, 1 and 1.5 mm. The slides were immersed in 2 mol l^{-1} HCl solution for 30 min, washed with deionised water, dried, immersed in acetone for 30 min and then dried in air. The slides were finally left at 550°C for 24 h to complete the cleaning process.

To prepare the nanocomposite, a glass slide was initially immersed in 20 ml of a solution containing 2 mol l^{-1} HCl and 5 ml of aniline for 3 h. Afterwards, it was washed with large amounts of deionised water to remove any monomer traces from the glass surface. Finally, the aniline retained inside the pores of the glass was chemically polymerised by immersing the slide for 30 min in 20 ml of a 2 mol l^{-1} HCl solution, containing 0.15 g of ammonium persulphate.

The sensor was constructed by fixing a Pani–PVG slide onto the distal end of a bifurcated optical fibre bundle (Oriel 77533), with a cyanoacrylic resin.

2.3. Instrumentation

The instrumentation employed in this work is similar to those described elsewhere [35]. It comprised a radiometric source (Oriel 6883), furnished with a quartz-halogen lamp (12 V, 100 W), whose radiation was modulated by an optical chopper (Oriel 75512) and focused onto one arm of the optical fibre bundle. The other arm was connected to the entrance slit of a monochromator (Oriel 77250). The reflected radiation was detected by a photomultiplier tube (Oriel 77340), connected to a lock-in amplifier (Stanford Research SR510), which was synchronised with the chopper frequency. A PC-AT 486 microcomputer, furnished with an ACL-8111 (ADLink Technology) parallel interface and a software written in Microsoft VisualBasic 3.0, was employed to control the monochromator and the lock-in amplifier and for the acquisition and treatment of data.

The measurements were made in a cell, whose temperature was controlled within ±0.2°C by employing a thermostatic bath (Quimis Q.214.D2).

3. Results and discussion

The preparation and characterisation of the Pani–PVG nanocomposite have been already described in details by Zarbin et al. [31]. When a PVG slide is immersed in acidic solution of aniline, the monomer, after diffusion through the pores of the glass, is adsorbed onto the surface as anilinium cation. By immersing the impregnated glass in a solution of ammonium persulphate, its colour changes gradually to dark green, indicating the formation of the Pani in the conducting state (emeraldine salt).

The colour of the glass is pH dependent, as the protonated and non-protonated forms of the Pani have different spectral characteristics [14,19,32]. Fig. 1 shows typical reflectance spectra obtained in solutions with different pH, employing a sensor constructed with a slide of 0.5 mm of thickness. As can be noted, the diffuse reflectance intensities decrease in the 450–600 nm region as the pH is increased, reflecting the colour change from green (acidic solution) to blue (basic solution). Fig. 2 shows the curve of reflectance intensities, normalised as described before [36], measured at 509 nm, as a function of pH. Although, a linear behaviour from pH 7.4 to 9.5 ($r = 0.9984$) has been found, the sensor would be employed to determine pH of solutions over a wider range (6–11), since methods of multivariate calibration based on artificial neural network can be used to extend the useful range of the sensor [37]. The dynamic range showed by the sensor described in the present work is similar to those obtained with a sensor based on poly(*o*-methoxyaniline) immobilised in cellulose acetate, evidencing that, in these cases, the support matrix does not affect the optode response, which is due to the protonation–de-protonation of the polymer. This dynamic range, slightly wider than those showed by single dye-based optodes, can be explained based on the fact that the Pani is a polyelectrolyte, having several acid sites with distinct pK_a's [20].

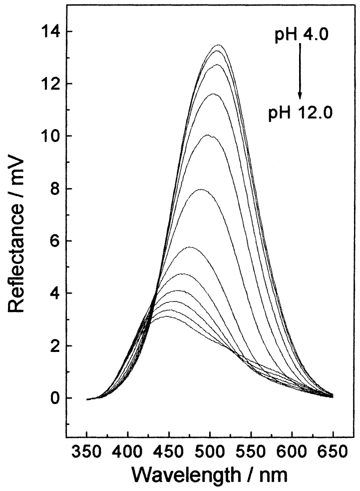

Fig. 1. Reflectance spectra obtained in solutions with different pH's employing the sensor based on Pani–PVG nanocomposite (slide thickness of 0.5 mm).

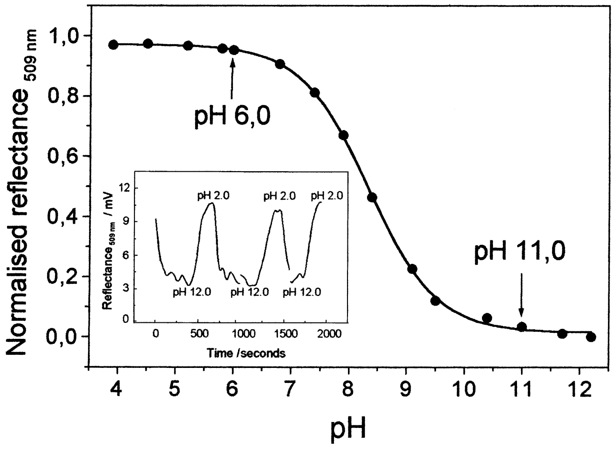

Fig. 2. Normalised reflectance curve measured at 509 nm as a function of pH.

The reversibility of the Pani–PVG nanocomposite was assessed by immersing alternately the sensor into solutions of pH 2 and 12, which provided reflectance signals equal to 10.5 ± 0.4 and 3.4 ± 0.1 mV (average of three measurements), respectively. These results confirm the reversibility of the sensor, as shown in the inset of the Fig. 2.

The colour change of the glass occurs from the solution interface towards the surface in contact with optical fibre tip, as the hydrogen or hydroxyl ions diffuse through the pores in this direction. Therefore, the interval of time required to make the nanocomposite homogeneously coloured, that is, to achieve a steady state signal, depends on the glass thickness. Fig. 3 shows sensor responses as a function of time when sensors of thickness' of 0.5 mm (a) and 1.5 mm (b), previously in a solution of pH 12, were immersed in a solution of pH 2. Response times of 3–5 min, 5–10 min and >16 min were obtained for slide thickness' of 0.5, 1 and 1.5 mm, respectively, when signal intensities were measured at 90% of the steady state. It is worth to mention that slower response time showed by the thinner slide during the first minute is probably due to minuscule air bubbles created on the surface of the sensor when it was immersed in the buffer solution. As could be expected, the response time is proportional to the thickness of the glass and sensors with faster responses could be constructed by employing thinner glasses. However, slides with thickness smaller than 0.5 mm were very fragile and produced optodes with very short lifetime. Therefore, 0.5 mm thick slides were employed, unless specified otherwise.

Measurements carried out in the linear pH range employing two sensors prepared with different slides provided

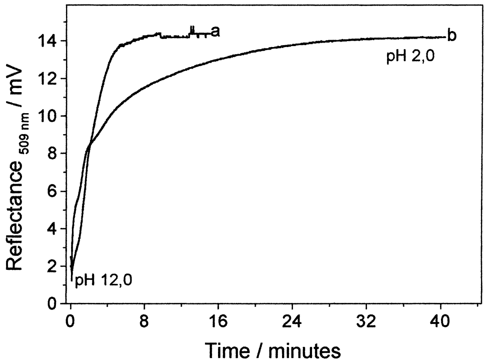

Fig. 3. Response curves as a function of time for optodes constructed with glass slides with thickness' of: (a) 0.5 mm; (b) 1.5 mm.

similar curves. For instance, the differences observed between the normalised reflectance intensities obtained for buffer solutions by employing these two sensors were always smaller than 12%, indicating that sensors could be prepared with reasonable reproducibility. However, no further experiments were performed in order to assess the actual reproducibility in the sensor preparation, as eventual drawbacks that would arise concerning the aspects of reproducibility can be easily overcame due to the long lifetime of the sensor, as will be described later.

The influence of the temperature on the optode response was studied in the range from 20 to 40°C, as shown in Fig. 4. Although, the temperature does not affect significantly the dynamic range of the sensor, it seems to cause some difference in signal intensities in the region comprised between pH 8.5 and 9.5, leading to a dynamic range slightly wider as the temperature is increased. These differences between reflectance intensities can be originated from the pH changes of the buffer solutions and the sensor behaviour due to the variation in temperature. Therefore, for analytical purpose, the sensor should be properly calibrated with buffer solutions whose pH have been determined at the temperature employed to perform the experiments.

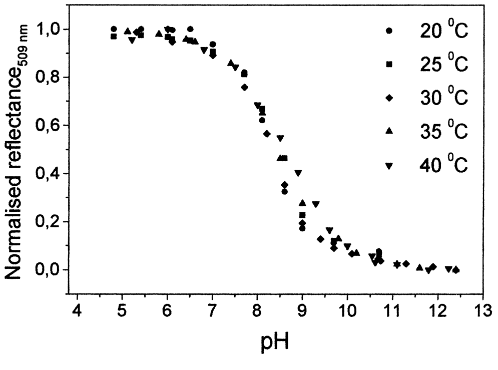

Fig. 4. Influence of the temperature on the sensor response.

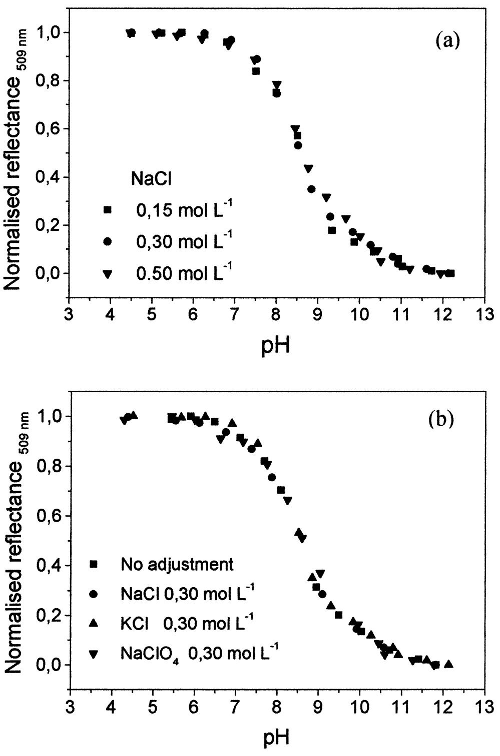

Fig. 5. Effects of the ionic strength and the nature of the ions on the sensor response. Analytical curves obtained with buffer solutions, in which were added: (a) 0.15, 0.30 or 0.50 mol l^{-1} NaCl; (b) 0.30 mol l^{-1} NaCl, KCl or NaClO$_4$.

The effects of the ionic strength and the nature of the ions were also verified, using buffer solutions in which different salts (NaCl, KCl and NaClO$_4$) were added in concentrations of 0.15, 0.30 and 0.50 mol l^{-1}. Fig. 5a and b show the analytical curves obtained by using NaCl (in different concentrations) and NaCl, KCl and NaClO$_4$ (0.30 mol l^{-1}) to adjust the ionic strength of solutions, respectively. Considering the curve obtained without ionic strength adjustment, as shown in Fig. 5b, these results indicate that both ionic strength and the nature of the ions have minor influence on the sensor response. Similar results were obtained when KCl and NaClO$_4$ solutions of different concentrations were employed to adjust the ionic strength. This behaviour of the Pani–PVG nanocomposite is probably due to the structure of the emeraldine salt, which has a highly conjugated π system [38], imparting a high charge density to this form of Pani. This high charge density on the surface of the polymer would explain the slight influence of the ionic strength of the solution on the optode response that is in accordance to the results obtained by Wolfbeis and Offenbacher [13].

Finally, the sensor lifetime was evaluated by storing it in a 1 mol l^{-1} HCl and performing monthly analytical curves in the pH range of 4–12. Similar curves were obtained even after 5 months. For instance, the normalised reflectance for the pH 8 buffer solution decreased from 0.77 to 0.66 after this period of time. The long lifetime of the sensor is a consequence of the minor leaching of the Pani entrapped in the porous cavities of the PVG and can be further increased if measurements are made in solutions of pH below 10, as basic solutions attack the glass.

4. Conclusions

The results obtained in this work indicate that Pani–PVG nanocomposite is suitable for the construction of optical pH sensors. As long as the polymer is formed inside the pores of the glass, cross-linking and structural defects are avoided, leading the formation of well-orientated chains. In addition, the polymer is less prone to leach. Therefore, nanocomposites can be produced with good reproducibility and long lifetime. As Pani possesses several acid groups with distinct pK_a's, the sensor shows an extended dynamic range and its response is only slightly influenced by ionic strength of the medium, since the emeraldine salt presents a highly charged surface.

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