

Review

## Review on State-of-the-art in Polymer Based pH Sensors

Olga Korostynska <sup>1</sup>, Khalil Arshak <sup>1,\*</sup>, Edric Gill <sup>2</sup> and Arousian Arshak <sup>2</sup>

1 Electronic & Computer Engineering Department, University of Limerick, Limerick, Ireland

E-mail: khalil.arshak@ul.ie

2 Physics Department, University of Limerick, Limerick, Ireland

\* Author to whom correspondence should be addressed: Electronic & Computer Engineering Department, University of Limerick, Limerick, Ireland, Tel: +353 61 20 22 67; Fax: +353 61 33 81 76

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**Abstract:** This paper reviews current state-of-the-art methods of measuring pH levels that are based on polymer materials. These include polymer-coated fibre optic sensors, devices with electrodes modified with pH-sensitive polymers, fluorescent pH indicators, potentiometric pH sensors as well as sensors that use combinatory approach for ion concentration monitoring.

**Keywords:** conductive polymer, pH measurement, response mechanism, sensor application.

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### 1. Introduction

Hydrogen ion is ubiquitous species encountered in most chemical reactions [1]. It quantified in terms of pH –the negative logarithm of its activity:

$$\text{pH} = -\log a_{\text{H}^+} \quad (1)$$

The pH sensors are widely used in chemical and biological applications such as environmental monitoring (water quality), blood pH measurements and laboratory pH measurements amongst others.

The earliest method of pH measurement was by means of chemical indicators, e.g. litmus paper that changes its colour in accordance to a solution's pH. For example, when litmus is added to a basic

solution it turns blue, while when added to an acidic solution the resultant colour is red. Since many chemical processes are based on pH, almost all aqua samples have their pH tested at some point. The most common systems for pH sensing are based upon either amperometric or potentiometric devices. The most popular potentiometric approach utilises a glass electrode because of its high selectivity for hydrogen ions in a solution, reliability and straight forward operation. Ion selective membranes, ion-selective field effect transistors, two terminal microsensors, fibre optic and fluorescent sensor, metal oxide and conductometric pH-sensing devices have also been developed [2, 3]. However, these types of devices can often suffer from instability or drift and, therefore, require constant re-calibration. Although litmus indicators and other above-mentioned pH sensors are still widely used in numerous areas, considerable research interest is now focused on the development of chemical or biological sensors using functional polymers. One may refer to a comprehensive review on the application of polymers in various sensor devices [4] and more specifically, review of various methods used for pH measurement [5].

By introduction of functional groups, polymers can be designed to selectively swell and shrink, thereby changing mass and elasticity, as a function of analyte concentration. The ion-exchange properties of conducting polymers are of special interest for potentiometric sensor development [6, 7, 8]. Conducting polymers are ideally suited for sensor applications because they not only exhibit high conductivity and electroactivity but they could also be used as a general matrix and can be further modified with other compounds in order to change selectivity [9]. Compared to conductive polymers, nonconductive polymers usually have a high selective response and a high impedance, which is important for eliminating interference by other electroactive species [10].

## 2. Polymers and Methods Used for pH Measurements

### 2.1. Optical and Fluorescent pH sensors

Optical methods can be used to measure the concentration or the activity of hydrogen ions. The basic concept of the optical methods of pH measurement relies on the fact that the incident beam of light is passed through a light guide to the active end of the sensor where it interacts with the chemical indicator, which alters the beam's intensity, usually by absorption or by fluorescence [1]. The modified optical signal is guided to the detector. The indicator is usually confined to the surface of the optical sensor or immobilized in an adjacent layer. J. Janata discussed the principal limitations of optical and electrochemical measurements in [1]. The application of the optical chemical sensors that are based on photoluminescence measurements in biotechnology and biomedicine offers tremendous advantages compared to conventional systems [11].

Several fibre-optic pH sensors have been proposed, which base their working principle on the fluorescence or the absorption of an appropriate chromophore [12]. Remote sensing can be achieved since the optical signal can be carried over long distances. Most of the reported fibre optic pH sensors exploit indicator dyes, which when immobilized on part of the optical fibre, cause pH sensitive changes in the absorption spectrum of the test solution [13]. Interaction with the analyte leads to a change in the optical properties of the reagent phase, which is probed and detected through the fibre optic. A major issue with this approach is the sensitivity of the device, which is directly related to the

thickness of the pH sensitive layer. Covalent chemical linking or simple physical encapsulation techniques can be used to immobilize dye molecules. Reportedly, surface modification of the optical fibres or substrate is required for covalent attachment of dye molecules, which results in excellent immobilization of the pH-sensitive dye [14, 15, 16]. Microspheres of polyacrylamide containing bound phenol red and smaller polystyrene microspheres for light scattering were packed in an envelope of cellulosic dialysis tubing at the end of a pair of plastic optical fibres [17]. The probe measured pH over the physiological pH range of 7.0 to 7.4 with 0.01 pH resolution and this flexible construction was about 0.4 mm in diameter. However, these methods are often more difficult to implement and may lead to loss of dye sensitivity or result in poor fluorescence properties. Non-covalent immobilization techniques for pH sensors have involved methods of entrapment behind semi-permeable membranes and adsorption within polymeric supports [18, 17]. As a drawback, coatings based upon non-covalent methods of dye immobilization suffer from leachability, making long-term *in vivo* use impractical. Hollow fibre membranes were also used in the development of extremely small diameter (0.22 mm) probe and catheter-type pH and pCO<sub>2</sub> sensors [15].

Grant and Glass [18, 19] used a sol-gel encapsulation of a pH sensitive self-referencing dye, seminaphthorhodamine-1 carboxylate, which resulted in a response time of 15 sec and good device sensitivity. This sensor was part of a system developed for blood pH monitoring of stroke patients, where such sensors are threaded through a catheter up to an occlusion in the vascular system of the brain to provide an indication of brain tissue viability. Brain pH decreases from a normal pH of 7.4 to a pH of 6.75 during the brain insult and a continuous monitoring system would be beneficial in the treatment of comatose neurosurgical patients and those who have suffered traumatic brain injury, hypoxic, ischemic brain insult and so forth [20].

The pH sensing properties of polyaniline (PANI), which belongs to the group of organic conducting polymers, were explored by Tsai et al [21]. The use of PANI receives attention due to its high conductivity, ease of synthesis, and its stability under ambient conditions. Fig. 1 depicts the spectral response in the pH range from 2.15 to 12.54 of PANI film deposited onto ITO glass employing constant-potential (0.80 V) electropolymerization [21]. These pH-dependent spectral variations of PANI films were explained by their transformation from the protonated to the unprotonated form.

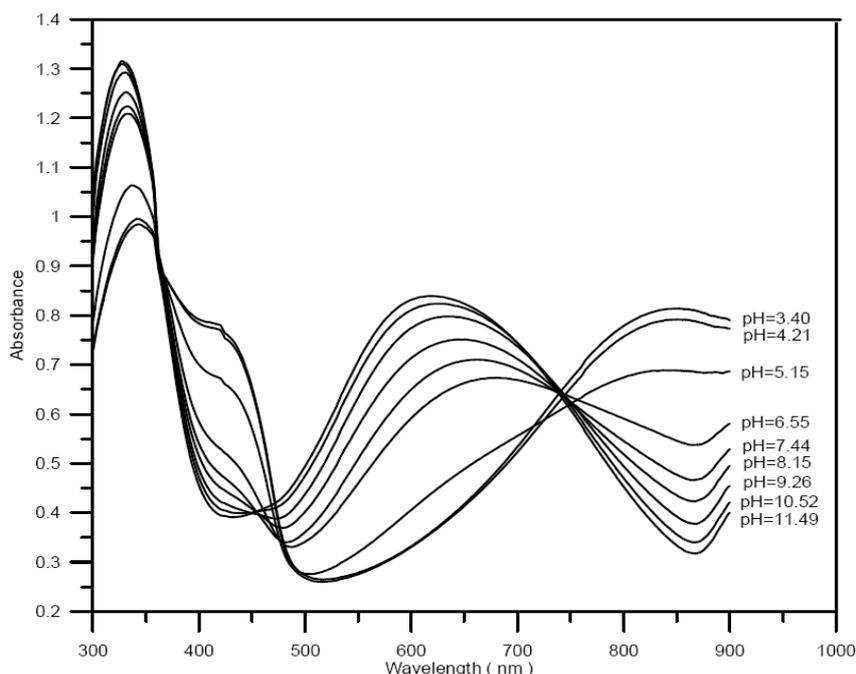
A novel method for pH measurements between pH 7.5 and 10.4 with a precision of 0.2 pH unit was reported in [22]. The method combines Raman spectroscopy and the automated sequential injection analysis system (SIA) and makes use of the acidbase properties of a commercially available water dispersion of PANI nanoparticles with a mean particle size of 46 nm. The pH measurements were conducted with the 633-nm laser excitation wavelength by calculating the difference between the Raman intensities of the primary and reference wavenumbers, where the pH-sensitive CH=CH stretching band at 1422 cm<sup>-1</sup> and C-H in-plane bending band of the quinoid form at 1163 cm<sup>-1</sup> were chosen as the primary wavenumbers [22]. Lindfors et al [23, 24, 25, 26] conducted in-depth fundamental studies of optical pH sensitivity of PANI conductive polymers and the research is ongoing.

Fluorescent pH indicators represent a valuable option for the determination of intracellular pH (pH<sub>i</sub>). A wide range of organic dyes with pH-dependent optical properties is available for pH<sub>i</sub> monitoring by means of fluorescence microscopy or other techniques relying on cell fluorescence analysis [27, 28, 29, 30]. pH indicators are weak acids with distinct spectral properties associated with

their protonated (HD) and unprotonated (D) forms. HD and D concentrations are related by the Henderson–Hasselbalch Eq (2):

$$pH = pK_a + \log \frac{[D]}{[HD]} \quad (2)$$

where  $K_a$  is the acid dissociation constant,  $pK_a$  is  $-\log K_a$ , and square brackets indicate concentrations [30].



**Figure 1.** Set of absorption spectra recorded for PANI film in buffer solutions of different pH.

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Examples of commonly used optically active molecular indicators for intracellular pH sensing are: 6-carboxyfluorescein, 2',7'-bis-(2-carboxyethyl)-5-(and-6)-carboxyfluorescein, 1,4-dihydroxyphthalonitrile, 8-hydroxypyrene-1,3,6-trisulfonic acid (HPTS), 1, seminaphthorhodafluor (SNARF)/seminaphthofluorescein (SNAFL) dyes, boron-dipyrromethene (KBH-01) [31, 32, 33, 34, 30, 35, 36, 37, 38, 39]. A shift of the emission peak as a function of pH was observed from 587 nm for pH 7.25 to 605 nm for pH 6.3 for dual-emission fluorophore C-SNAFL-1 in [31]. The pH mediated intra-molecular association and inter-molecular aggregation of a range of amphiphilic poly(l-lysine iso-phthalamide) polymers have been investigated in aqueous solution over a range of pH values and concentrations by Dai et al [35]. The desired functionality of these bioresponsive amphiphilic polymers was achieved by incorporating pendant hydrophilic carboxyl groups along the polymer backbone, via the l-lysine moiety, balanced by a degree of hydrophobicity introduced via the iso-phthaloyl moiety. Incorporation of low levels of bis-functional Cy3 (poly-Cy3) and/or Cy5 dye (poly-Cy3/5 or poly-Cy5) co-monomers in the responsive polymer backbone allowed detailed probing of the pH mediated hydrophobic association using a combination of optical spectroscopic techniques. Both steady-state fluorescence spectroscopy and fluorescence lifetime measurements of poly-Cy3 revealed a

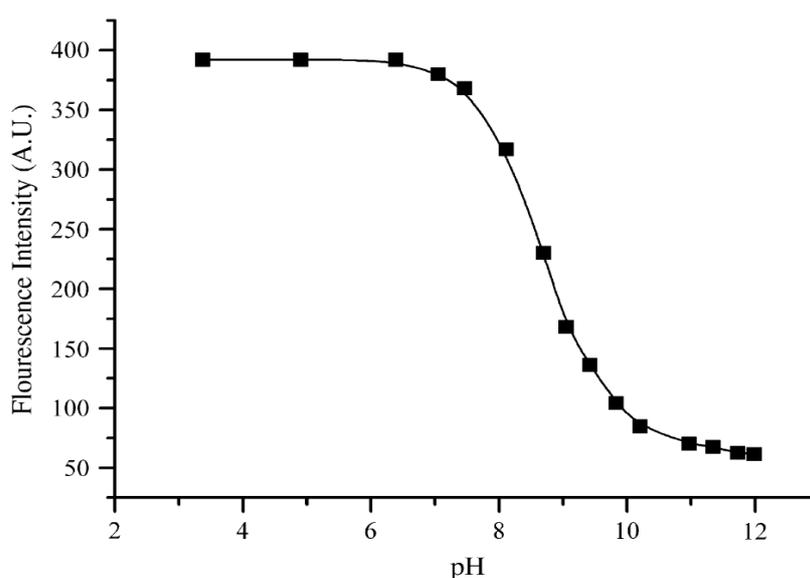
conformational transition at pH 4.5, below which the polymer collapsed into a compact globular structure (hypercoil) bringing the fluorophore molecules into close proximity with one another. This resulted in a dramatic reduction in fluorescence intensity and fluorescent lifetime in the single fluorophore systems (poly-Cy3) accompanied by a red shift in the maximum emission wavelength. Observed red shifts in the emission maxima and enhancements of fluorescent lifetimes with increasing polymer concentration suggested the formation of polymer aggregates [35].

The nano-pH sensor based on dual-fluorophore-doped nanoparticles that offers the advantages of adequate sensitivity, accuracy and rapid detection of pH was proposed by Gao et al [36]. Additionally, this sensor showed excellent stability, high reproducibility and a fast response time. The development of a pH-sensitive fluorescence nano-sensor by co-doping the indicator dye and reference dye in silica nanoparticles is considered due to their biocompatibility.

Spectral analysis by chemometric methods was applied to optical pH sensing with aminofluorescein as fluorescent indicator in [11]. This method was found to be superior to the ratiometric dual-wavelength detection, when the pH value influences the spectrum in a complex way. In the case of aminofluorescein, the range of measurement is extended compared to the ratiometric method. The pH value can be calculated from the fluorescence spectra of the indicator independently of the absolute intensity and of the temperature of the sample [11].

Carboxynaphthofluorescein (CNF) and ETH 5350 pH sensitive dyes are ratiometric, meaning that the spectrum of the fluorescence has two peaks and the ratio between these peaks changes as the pH levels change. The large alteration in the optical properties of ETH 5350 coating were monitored as a result of pH change from pH 2.0 to pH 11.5 [40].

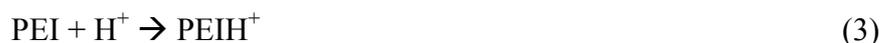
Novel complex polymers with improved pH sensing properties are constantly emerging, thanks to the hard work of chemists all over the world. As an example, one may refer to the paper by Bojinov et al [41], where the fluorescent properties of a number of polymers were explored in terms of their pH sensitivity. Fig. 2 shows the changes in the fluorescence emission spectra of 1,2,2,6,6-pentamethyl-piperidin-4-ol as a function of pH.



**Figure 2.** Effect of pH on fluorescence intensity ( $\lambda_{\text{ex}} = 370$  nm) of 1,2,2,6,6-pentamethyl-piperidin-4-ol. Reprinted from [41] © 2007 with permission from Elsevier.

## 2.2. Electrodes modified with pH-sensitive polymers

It has been shown that electromodified electrodes with conducting polymers could act as good candidates for replacement of popular glass pH electrodes [10]. The examples of pH chemical sensors using polymer-film-coated electrodes include electropolymerization of pyrrole, aniline, thiophene, or benzene derivatives [10, 42, 43, 44, 45]. However, the measurements of pH using the above-mentioned conductive polymers had poor reliability due to defects and pinholes present in the films structure. Herlem et al [10] reported a pH sensor, where a smooth Pt electrode was coated with an electrically insulating polymer, namely linear polyethylenimine (L-PEI). Platinum electrodes, modified by a coating of a thin L-PEI film, resulting from the anodic oxidation of pure ethylenediamine, exhibited a linear, reversible, and stable in time potential response sensitive to pH changes in aqueous media. The assembly of the electrode surface coated with electropolymerized ethylenediamine acted as a transducer of the electrode potential versus the pH value in aqueous solutions. A possible mechanism by which the linear polyethylenimine responds to pH changes could be due to the affinity of the numerous amino groups to the protons in solution. The reaction of  $H^+$  with amino groups creates local charge density excess at the electrode surface. The potentiometric response can be considered as behaviour controlled by a surface reaction, which takes place on the PEI film. Protonation and deprotonation of superficial amino groups of the PEI is symbolically described in Eq. (3) [10]:



When equilibrium is reached at the PEI/solution interface, then the equilibrium expression  $K$  of the surface reaction is determined by Eq. (4) [10]:

$$K = [PEIH^+] / ([PEI] [H^+]) \quad (4)$$

Herlem et al [10] also reported that as the film thickness increases, the more amino groups are present, and thus the pH sensitivity of the modified electrode increases. These thick film modified electrodes give repeatable pH responses, independent of direction of pH change, and give consistent results when the pH value is varied in a random manner.

Another example of wire electrodes coated with pH-sensitive polymers, fabricated by galvanostatic electrochemical polymerization of monomers, namely, pyrrole (Py), 3-(2,5-dihydroxybenzyl)pyrrole (PyQH), aniline (An) and o-phenylenediamine (oPD) can be seen in [9]. The polymers were synthesized with perchlorate or bovine serum albumin (BSA) dopants in a propylene carbonate or universal buffer electrolytes, respectively. The potentiometric characteristics of the resulting films show sub- to near-Nernstian responses. The range of electrode sensitivities (at a temperature of 25 °C) for the four polymers used are -43.2 mV/pH for PPy, -46.0 mV/pH for PPyQH, -42.1 mV/pH for PAN and -50.7 mV/pH for PoPD [9]. All have a linear working range of pH 3 to pH 10 and an average response time of 3 to 5 min.

The doping and supporting electrolyte anions' effect on the potentiometric sensitivity and response time of polypyrrole (PPy) electrodes towards changes of solution pH were studied in [6]. It was found that the response of PPy doped by easily exchangeable common anions ( $Cl^-$ ,  $NO_3^-$ ,  $ClO_4^-$ ) in their solutions (KCl,  $KNO_3$ ,  $NaClO_4$ ) is slow. In contrast, polypyrrole films deposited in the presence of

weak acid anions, such as phthalates, oxalates and salicylates, were characterised by instantaneous pH responses in these solutions.

The redox and charge transport properties of an electropolymerized N-substituted phenazine, polyphenosafranin (PPS) polymer film was interpreted as the diffusion-migration of electrons and ions [44]. Electron transport occurs via a process of sequential electron self-exchange between neighbouring redox sites. The theory for the faradaic impedance of redox polymers was proposed by Mathias and Haas [46]. Electron transfer at the electrode-film interface is accompanied by the ingress of charge-compensating counter-ions to or from the film. When polymers including electroactive nitrogen atoms are reduced, either anions are released from the polymer, or protons are incorporated into it. Electron transport occurs via a process of sequential electron self-exchange between redox sites. Because it is accompanied by intermolecular proton transfer, deprotonation of the polymer may reduce the homogeneous electron-transfer rate constant [44].

A pH sensor utilizing a redox-active copolymer has been reported by Robinson and Lawrence [2], where the response of vinylanthracene, vinylferrocene, and poly(vinylferrocene) has been analyzed and compared with the response of the p(VA-co-VF) copolymer. The results showed the presence of both poly(vinylferrocene) and poly(vinylanthracene) within the copolymer. The voltammetric response of p(VA-co-VF) has been analyzed over the pH range 4-9 and over a wide temperature scale.

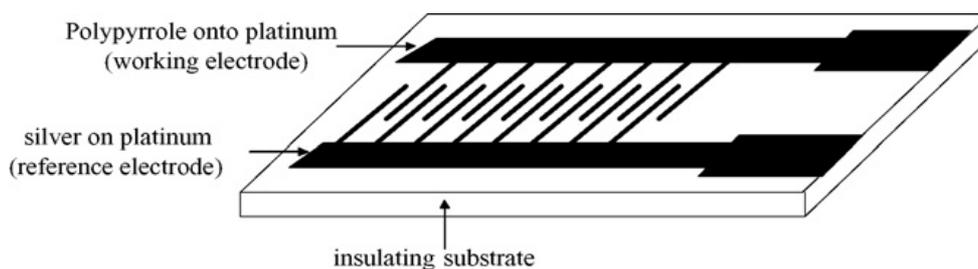
### 2.3. Potentiometric pH sensors

Routinely used ion-selective electrodes (ISEs) for the determination of blood electrolytes have a market size comparable to that of glass electrodes. The lower detection limit and the discrimination of interfering ions (the selectivity coefficients) have been improved during the past decade by factors up to  $10^6$  and  $10^{10}$ , respectively, thus allowing their application in fields such as environmental trace analysis and potentiometric biosensing [47]. ISEs and their optical counterparts, ion-selective bulk optodes, have the unique capability of sensing free ion activities instead of the total concentration. Bulk optodes belong to a newer class of sensors and are usually based on the competitive or cooperative extraction of the analyte ion with protons between the polymeric and aqueous phase [48]. This two-phase sensing mechanism has advantages in reaching a lower detection limit dictated by the thermodynamics ion extraction, and may lead to the mass production of monodisperse ion sensing microbeads that can be flexibly coupled with analytical flow cytometry or optical-fiber based microsensor arrays [49, 50, 51]. The unique ion-sensing capabilities of ISEs and bulk optodes make them very useful for clinical diagnosis, drug analysis and environmental monitoring.

Various polymers have been considered suitable for potentiometric pH sensors [52, 53, 54, 55, 56, 57]. Potentiometric pH sensors based on linear polyethylenimine (L-PEI) and linear polypropylenimine (L-PPI) (two synthetic enzymes and biocompatible polymers) films were prepared by electropolymerization of three different monomers: ethylenediamine (EDA), 1,3-diaminopropane (1,3-DAP) and diethylenetriamine (DETA) in order to be used in clinical, dermatological and biological applications, such as *in vivo* analysis [53]. These polymers are considered good candidates for pH biosensors due to their strong bonding to the electrode surfaces during the electropolymerization step.

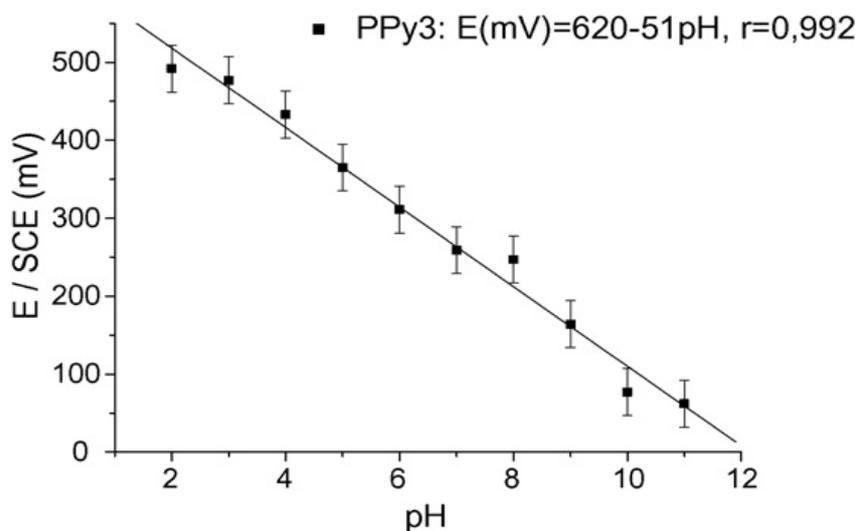
The effect of pH on polypyrrole chloride (PPy/Cl), polypyrrole vinyl sulphonic acid (PPy/PVS), polyaniline chloride (PAn/Cl) and PPy/PVS PAn/Cl composites was explored in [42]. In acidic media, polyaniline (PAn) can be oxidized and reduced from a more conductive (oxidized) to a less conductive (reduced) form; deprotonation of the polymer at high pH results in decreased conductivity. The conductivity of polypyrroles (PPys) in the oxidized form is also known to be pH dependent with resistance increasing dramatically above pH 12.

Potentiometric pH miniaturized sensors based on electrosynthesized polypyrrole films were recently developed by Lakard et al [57]. These pH sensors have two interdigitated microelectrodes, fabricated by photolithography. One electrode of the sensor is coated by a polypyrrole film, while the other one is coated by a silver film used as reference electrode, as shown schematically in Fig. 3.



**Figure 3.** Schematic drawing of interdigitated microarray electrodes. Reprinted from [57] © 2007 with permission from Elsevier.

Four sensors with various film thicknesses were tested for pH response, where the samples have film thicknesses of: PPy1 – 150 nm, PPy3 – 400 nm, PPy10 – 1750 nm and PPy15 – 2400 nm. The potentiometric response of the sensor with 400 nm polymer film to pH values is illustrated in Fig. 4.



**Figure 4.** Potentiometric response to pH changes of the sensor coated with PPy films (average values are given after five measurements, bars correspond to standard deviations).

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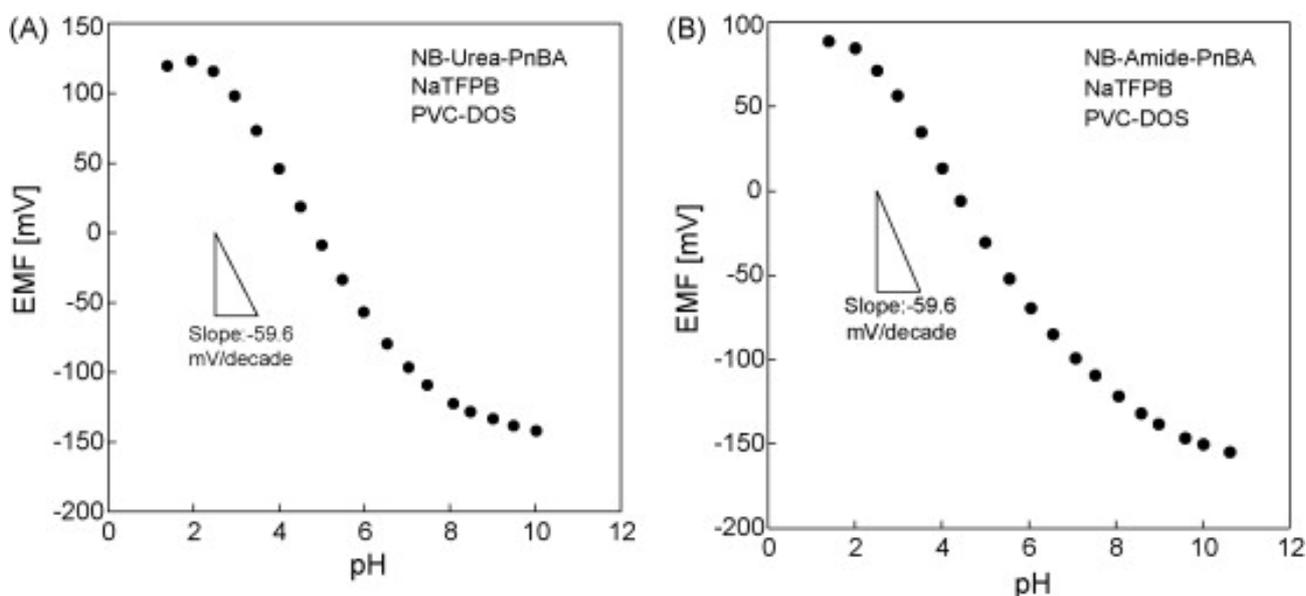
The measured potential as a function of pH and the linear correlation coefficient ( $r$ ) of the linear regression  $E = f(pH)$  is given in the inset of Fig. 4 [57]. One may conclude that the potentiometric

response of this sensor is linear to pH changes for the pH range between 2 and 11. The long-term stability was assessed and during 30 days no deterioration in the sensor performance was noted.

Potentiometric pH measurement using a neutral carrier membrane placed on a conducting polymer was employed by [58]. Conducting polymer coatings of 0.5  $\mu\text{m}$  thickness were deposited on a Pt electrode by electropolymerization from a solution consisting of 120 mg  $\text{LiClO}_4$  and 10  $\mu\text{l}$  Pyrrole dissolved in 5 ml acetonitrile. Electropolymerization was carried out in the galvanostatic mode with a current density of 5  $\mu\text{A mm}^{-2}$  and a polymerization time of 10 s. Finally, a drop of solution of a PVC-based neutral carrier membrane solution with trin-dodecylamine as proton carrier was put on the electrode with the aid of a micro-dispensing unit. The response of this pH sensor followed Nernstian law with a response time of less than 1 s. The potential drift was 250  $\mu\text{V}$  per day, which corresponds to a pH drift of 5/1000 pH units per day [58]. This device was one of the earliest tested *in vivo* pH and glucose sensors, manufactured using thin film technology on flexible polymer substrate. The research towards integration of multi-sensor head for simultaneous *in vivo* monitoring is ongoing.

Poly(vinylbenzylchloride-co-2,4,5-trichlorophenyl acrylate) (VBC-TCPA) spheres, approximately 725 nm in diameter, were prepared by dispersion polymerization then derivatized with diethanolamine to realize a mass changing pH-responsive polymer [59]. While the pH-responsive polymer spheres are suitable for use with any mass-sensitive sensor platform, in this work, the polymer spheres are combined with magnetoelastic thick films to achieve a remote query pH sensor. The magnetoelastic pH sensors were fabricated by spin-coating of aminated polymer spheres onto the surface of a magnetoelastic ribbon. The pH response of these sensors was examined by monitoring changes in sensor resonance frequency as a function of test-solution pH. The sensors demonstrated a linear pH response from pH 3.0 to pH 9.0, with a change in resonance frequency of 0.2% per pH unit for a 1.5- $\mu\text{m}$  thick polymer layer [59].

Recently published research [48] demonstrated a strategy for covalent grafting of fluorophores into a self-plasticized polymer matrix, and a plasticizer-free bulk optode microsphere sensor for sodium using the polymer-fluorophore composite. Two types of Nile Blue derivatives were synthesized by covalently grafting the Nile Blue structure into self-plasticized poly(n-butyl acrylate) via urea (NB-urea) or amide (NB-amide) linkers. Modification of n-butyl acrylate with a suitable functional group into the polymer backbone for polymerization was followed by the reaction with Nile Blue. The grafted NB-urea and NB-amide polymers prepared using this method can be used as fluoroionophore in ion selective optodes in the same way as commercial chromoionophores, but with improved lifetimes [60]. Plasticizer-free fluorescent ion-sensing microspheres were prepared using the two polymer-fluorophore composite for sodium, and showed good selectivity toward potassium, calcium and magnesium. The measuring ranges of sodium ions were found as  $10^{-1}$ – $10^{-4}$  M and  $1$ – $10^{-3}$  M, for NB-urea and NB-amide–PnBA, respectively, at physiological pH, as shown in Fig. 5. [48].



**Figure 5.** Potentiometric pH response of PVC–DOS membranes containing the two types of grafted Nile Blue derivatives, (A) NB-urea–PnBA (R2) and (B) NB-amide–PnBA (R2).

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#### 2.4. Miniaturized pH sensors

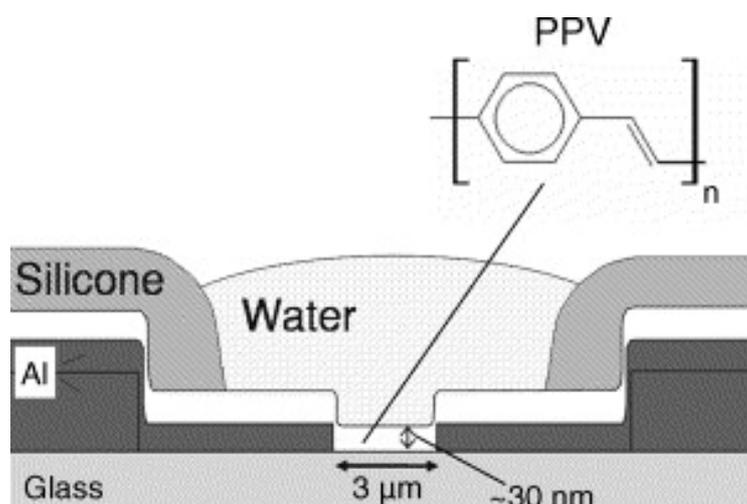
Advances in the semiconductor industry combined with novel recently developed polymer materials enable engineers to design various sensors with optimised performance parameters. Thong et al [61] reported a novel design of silicon piezoresistive pH sensors, based on a pH sensitive hydrogel, namely poly(vinyl alcohol)–poly(acrylic acid). The general sensor principle is as follows: swelling due to pH value changes causes bending in a flexible plate. In the case of capacitive transducers, a change in capacitance will be detected. For resistance bridge sensors, due to membrane deflection, the corresponding membrane stress will change the bridge resistance and consequently the output voltage.

Conventional electrochemical methods of determining the pH of body fluids have drawbacks. Newer optical methods offer the promise of miniaturisation and continuous *in vivo* measurements without drift. The ability of a holographic sensor based on a thin-film, biocompatible hydrogel (approximately 10  $\mu\text{m}$ ) of poly(2-hydroxyethyl methacrylate) and ionisable 2-(dimethylaminoethyl) methacrylate to accurately measure the pH of blood plasma *ex vivo* was investigated in [62]. It was found that the sensors behave in a fully reversible manner. After an initial calibration with buffers, they were able to measure pH over extended periods of more than 40 hours.

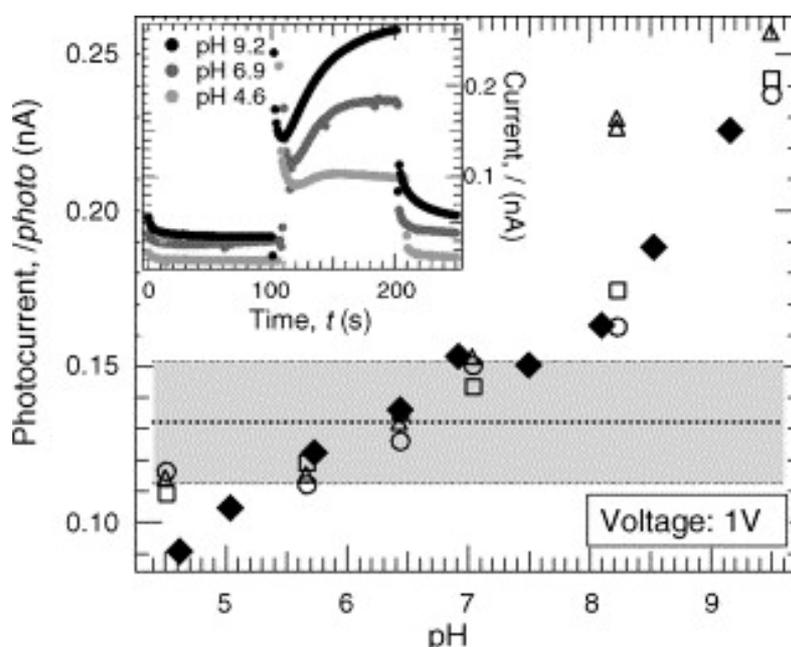
Patterns of polypyrrole (PPy) have been fabricated on flexible poly(tetrafluoroethylene) (PTFE) films using a combination of micro-contact printing, electroless deposition of copper and electropolymerisation of pyrrole [8]. A patterned elastomeric stamp was used to deliver a nitrogen-containing silane coupling agent to an argon plasma-pretreated PTFE surface. The surface was subsequently activated by  $\text{PdCl}_2$  and immersed in an electroless copper plating bath allowing selective metallisation. Electropolymerisation of pyrrole was performed on copper-patterned PTFE resulting in the formation of micrometer-scale PPy structures. Potentiometric measurements have demonstrated that PPy-patterned PTFE has potential application as a pH sensor.

Miniaturized pH biosensors were developed using a photolithography process to promote commercial applications. This method allowed the patterning of the metal electrodes on an oxidized silicon surface. A sputtering technique was chosen to coat the patterned electrodes with platinum. Then, one electrode was coated with a polymeric film while the other one was coated with silver to be used as reference electrode. Interdigitated array electrodes were patterned in order to increase the exchange surface between the polymer coated electrode and the solution being analysed. The polymer films coated on the platinum electrodes showed linear potentiometric responses to pH changes from pH 3 to pH 10. Resulting electrodes exhibited both reversibility and stability versus time. The effect of the different polymer film thicknesses to potentiometric responses was also studied [53].

Among the group of conjugated polymers, poly(*p*-phenylene-vinylene) (PPV) and derivatives are some of the most promising candidates for organic electronics applications. The delocalized  $\pi$ -electrons from the phenyl-rings and conjugated carbon chains are responsible for the semiconducting properties of PPV. It is generally believed that for polymers the primary photoexcitation results in the creation of excitonic states, rather than in the direct creation of free charge carriers as is the case for inorganic semiconductors. Fig. 6 shows a schematic drawing of a new pH-sensitive device that uses the photoconductive properties of a thin PPV layer reported by Pistor et al [63]. No device passivation was necessary since the applied voltages were below the threshold for electrolysis.



**Figure 6.** Schematic drawing of the pH sensitive device showing the aluminum contacts (dark grey) below a thin (30 nm) layer of PPV (white). In the wet state, a solution covers the whole area inside the pool formed by the silicone protection over the contact pads. Drawing is not to scale. Reprinted from [63] © 2007 with permission from Elsevier.



**Figure 7.** Variation of the photocurrent,  $I_{ph}$ , for different pH values. In the inset, the light responses of the devices exposed to phosphate buffer (100 mM) with pH values of 4.6, 6.9 and 9.2 are shown. In the main graph the photocurrents are plotted against the pH of the buffer solution for one device (filled symbols). Three different series of the same buffer solutions are measured using a second device (open symbols) to show reproducibility. The dotted line represents the average of the DI water control measurements made in between pH measurements, with its standard deviation represented by the grey band. Reprinted from [63] © 2007 with permission from Elsevier.

Fig. 7 illustrates the photocurrent,  $I_{ph}$ , measured in phosphate buffer solutions [63]. The inset shows the raw data measured at a voltage of 1 V for three different buffer solutions with pH of 9.2, 6.9 and 4.6. The response of the device to illumination increases with increased pH value, while the dark current is not significantly altered. For higher pH values, the photocurrent generally needed more time to reach saturation. The photocurrent (shown by filled diamonds) increases monotonically with increasing pH. This change of the photocurrent with respect to pH was found to be reversible; DI water control measurements oscillated around an average value of 132 pA with a standard deviation of 19 pA (represented in the plot by the dotted line with its standard deviation represented by the grey shading) [63]. The photocurrent showed a considerable increase in value from  $I_{ph} = 91$  pA at pH 4.62 to  $I_{ph} = 230$  pA at pH 9.16. Therefore, this device is strongly considered for pH-sensitive applications.

### 3. Conclusions

A broad range of methods and polymer materials employed for pH sensing is reviewed, with the focus on the latest literature reports. The choice of a particular polymer or method of pH measurement would depend on the targeted application along with sensitivity and selectivity requirements, set by the end-user.

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