

pH Sensing Materials for MEMS Sensors and Detection Techniques

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Abstract. This paper focuses on finding criteria to choose the best combination between a pH sensitive material and detection method. Various pH sensitive polymers and measurement methods exist. However, some measurement methods are not sensitive enough to measure pH in the presence of salt and this need to be investigated further. This paper discusses various pH sensitive materials and detection methods, their physical and/or chemical behavior, merits and demerits, applications etc. Our results show that certain materials can not only be detected by standard detection method but also with other detection techniques.

Keywords: pH sensors, MEMS, detection methods, pH sensing materials

1. Introduction

During last two decades micro system technology has been improved to great extent. MEMS sensors are used for various applications like military applications, video and photo cameras, games, automobiles, medical areas, industries etc. This paper discusses only pH sensing materials and their detections techniques. The use of pH measurement is mostly employed in bio and chemical labs. Most of the biological and chemical processes are dependent on pH so it is mostly used in lab measurements.

1.1. Why pH is important

pH has great importance in laboratory measurements because a lot of chemical and biological processes are dependent on pH.

- It is essential to measure pH to find the chemical characteristics of a substance. Both the speed or rate of chemical reactions and the solubility of chemicals or biomolecules are dependent on pH. So controlling pH is very important in order to optimize the desired reaction or to prevent unwanted reactions.
- The pH value of rivers, lakes and oceans depends on the type of plants and animals living there. The wastewater from factories changes the pH value of water so we can detect the presence of dangerous chemicals inside water.
- Process industries deals with pH measurements like food industries, drugs, textiles, semiconductors, cements etc.

1.2. What is pH?

pH is the combination of two words, p for power and H for hydrogen [1]. In an aqueous solution, the equilibrium exists between water, alkali (OH^-) and acid H^+



pH is the acidity or basicity of the material. The pH value can be written as mathematically.

$$\text{pH} = -\log a \text{H}^+$$

so the pH value is the negative logarithm activity of hydrogen ions [1].

pH is used to mention the degree of basicity or acidity of an aqueous solution at a given temperature. The term acidity shows that the pH reflects the amount of hydrogen ions and not the concentration of hydrogen ions. Normally the pH range is from 1-14. If the pH value is from 1-6 then the solution will be acidic, if the pH value is 7 then the solution will be neutral and if the pH value is from 8-14 then the solution will be basic.

2. Detection Techniques

There are many techniques to detect the pH. Traditional detection methods are pH test strips and glass electrode. Some other methods are ISFET, pH Image, Optical fibre, Magnetoelastic, Conductometric, Cantilever, Glass electrode and Potentiometric.

Based on these detection techniques, various pH sensors can be constructed depending on the requirements for different application techniques.

2.1. ISFET based pH sensors

ISFET stands for ion sensitive field effect transistor. ISFET sensor is based on new technology and is an alternative to glass electrode. The working principle is based on the fact that the drain current is an indicator of pH in the solution in which the ISFET is immersed. ISFET is glass-less and can be small sized due to its fabrication technology and is inexpensive device as compared to glass electrode. It can be battery powered and pocket sized pH measurement system [1]. ISFET devices are compatible with CMOS processes and can be realized with microelectronic technology. ISFET devices are used to measure the wide range of pH from basic to acidic solutions. ISFET devices in general use Si₃N₄ and Al₂O₃ as gate insulators.

2.2. pH image sensors

pH image sensors are used in various real time and chemical industrial applications. They are used to take two dimensional distributions and dynamic images of chemical variations. pH image sensor work on the charge transfer technique. CMOS (Complementary metal oxide semiconductor) circuit process technology can be used to fabricate pH image sensors. pH image sensors may have great importance in medical, biological and chemical industrial applications.

2.3. Optical fibre pH sensors

Optical fibre sensors have many advantages over other glass electrode methods for the measurement of pH like they have fast response and effects of ionic concentrations are negligible. Optical fiber pH sensors are based on color change principle of sensing polymer.

2.4. Magnetoelastic pH sensors

Magnetoelastic pH sensor is based on the principle of an efficient conversion between magnetic and elastic energies and vice versa. By changing the electric field in a coil, a magnetic field is induced, which cause vibration in a magnetoelastic ribbon like sensor. Magnetoelastic pH sensor consists of two coils (drive coil and pickup coil), magnetoelastic substrate, pH sensitive material deposited on substrate [3].

2.5. Conductimetric pH sensors

A conductimetric pH sensor is based on the measurement of the conductivity of a pH-responsive hydrogel and other materials. It is constructed by coating planar interdigitated electrode arrays with a photolithographically patterned hydrogel membrane [5]. The hydrogel sensing layer swells or shrinks to a hydration determined by the pH of a solution in which it is immersed. Sensing layer must respond to analyte of interest and produce a measureable change in the electrical properties.

2.6. Cantilever based pH sensors

Cantilever based pH sensor is a useful technique to measure the pH of aqueous solution. It is based on a cantilever attached with a piezoresistive.

Aqueous solution enters from inlet tube and cause the swelling or shrinking of the hydrogel depending upon the pH. When the pH of the solution changes, hydrogel swells or shrinks which cause the deformation of the cantilever. So by changing the shape of hydrogel, cantilever bend and this change is converted into the voltage with the help of piezoresistive. In this way the pH of the aqueous solution is measured.

2.7. Glass electrode pH sensors

pH of the solution is very difficult to measure directly. So the measurement of pH is done by comparing the potential of the solutions of known H ions with the solution of unknown H ions. The solution with known H ions is called reference solution. The potential between these two solutions is measured by using two cells. One is called reference half cell and the other is called sensing half cell.

2.8. Potentiometric pH sensors

In potentiometric sensors the signal is measured as potential difference (voltage) between the working electrode and the reference electrode. The working electrode's potential depends on the concentration of the analyte in the gas or solution phase. The reference electrode is needed to provide a defined reference potential. Potentiometric pH sensors consist of for example Pt/PtO₂, W/W₂O₃, Pb/PbO₂, Ir/IrO₂ etc [1]. pH sensitive material is applied on the working electrode and when the voltage is changed between the working electrode and reference electrode, that potential difference is measured. In this way the change in the pH can be measured. These sensors are very efficient over a wide pH range, at high temperature and pressure. The response time of these sensors are also fast as compared to other sensors.

3. List of pH sensing materials for sensors

List of few sensing materials for sensors are given below.

| No. | Material | Detection Method | Physics or Chemistry | Advantages | Disadvantages | Applications | Reference |
|-----|---|---|---|---|---|---|-----------|
| 1 | Allylamine hydrochloride (PAH) and poly(acrylic acid) (PAA) | Optical fibre (Optical fiber pH sensors based on layer-by-layer electrostatic self-assembled Neutral Red) | Optical, color change. Optical fiber sensor are based on evanescent absorption (pH range 3-9) | Fast response (10s) and high repeatability. | There are still too many unknown factors. | hydrophobic coatings, anti-corrosion protective overlays, anti reflection coatings, smart polymers for drug release, active microspheres, photovoltaic devices, OLEDs and also, sensors | [4] |
| 2 | cresol red, bromophenol blue and chlorophenol red | Optical fiber | Optical, color change. Optical fiber sensor are based on evanescent absorption pH 4,5-13 | No information | No test response to ions | Chemical, biomedical and environmental applications | [7] |
| 3 | Two Magnetoelastic thick film elements, one coated with pH and salt concentration sensitive mass changing polymer poly(acrylic acid- co-isoctylacrylate) (pAA-IOA), while the other is coated with poly(3-sulfopropyl methacrylate-co-isoctylacrylate) (pSPMA-IOA), and a polyelectrolyte gel | Magnetoelastic pH sensor | Mass change. In response to a magnetic query field the Magnetoelastic sensor mechanically vibrates at a characteristic frequency that is inversely dependent on the mass of attached polymer. | Cheap fabrication | No information | Biological, chemical and environmental applications | [3] |
| 4 | pAA-IOA, PEGD crosslinker, AIBN initiator | Magnetoelastic pH sensor | Mass change. In response to a magnetic query field the Magnetoelastic sensor mechanically vibrates at a characteristic frequency that is inversely dependent on the mass of attached polymer. | Cheap fabrication | No information | Biomedical applications | [6] |

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|----|--|---|--|--|--|--|-----|
| 5 | Polyaniline | Conducting polymer pH sensor | Potentiometric (Potential change by changing electrical impedance of electrodes). Polyaniline-based pH sensor with the nernstian slope 52.1 mV/pH and the linear dynamic range between 3.5 to 11.94 | Hydrofluoric acid don't influence the response of electrode | No information | Bio-medical applications | [1] |
| 6 | copolymer: HEMA + DMAEMA (9:1), TEGDA crosslinker (1.5%), DMPA photoinitiator, MPS adhesion promoter. 8 um layer | Conductimetric pH sensor, conductivity, interdigitated electrodes, Pt interdigitated electrode arrays | Potential change by changing electrical impedance of electrodes, pH 5-9, (4-10) | No information | No information | Medical and biological applications | [8] |
| 7 | Amorphous boron carbon nitride (a-BCxNy) | ISFET based pH sensors | The pH sensitivity increased with increasing carbon contents of the a-BCxNy sensing membrane and reached a maximum of 46 mV/pH for the carbon concentration of 47%. The response of these sensors is closed to 6s. | The drain current which is an indicator of pH, remained stable over a period of 10 min in the phosphate solution with varied pH. | Difficult to control, varying time to time | Biosensor microchip applications | [1] |
| 8 | Boron-doped silicon nano-wires (SiNWs) | ISFET based pH sensors | The response of the conductance of APTES-modified SiNWs to changes in solution pH shows that this pH dependence is linear over the pH 2-9 range. | Small size and capability of nanowires for sensitive, label free and the real time detection of a wide range of bio-chemical species | No information | Bio sensors, array based analysis and vivo diagnostics | [1] |
| 9 | Si3N4/SiO2/Si structure | pH image sensor | Ion sensitive (Array of ISFET sensors). The acid or base distribution on the dentin surface was detected as pH value and concerted as pH images. | Images of pH distribution | Time varying | For the surface analysis of curious dentin from extracted human teeth. | [1] |
| 10 | Poly(methacrylic acid)(PMAA) with poly(ethylene glycol) diamethacrylate | Nano-Constructed cantilever-based pH sensor | Expansion and reversible change in surface stress causing the micro-cantilever to bend | Highly sensitive, low power, and compact transducers | No information | No information | [1] |
| 11 | Mercaptohexadecanoic acid (MHA) and hexadecanethiol (HDT) | Nano-Constructed cantilever-based pH sensor | Changes in interfacial stress between thiol-covered cantilevers and buffer solutions of various pH occur. The difference in response (MHA minus HDT) shows a net signal that can correlated with pH value. | Extremely small size (<<0.1mm ²) which allows cheap mass produced fabrications using IC technology. | No information | Medical and biological applications | [1] |
| 12 | Pt/PtO2 | Metal oxide pH sensor | Potentiometric (the electrical potential of the electrode is sensitive to pH) | 1) Good stability over a wide pH range even at high temperature, high pressure and aggressive environment, 2) fast response | No information | Used to develop a pH electrode at high temperature and high pressure | [1] |
| 13 | W/W2O3 | Metal oxide pH sensor | Potentiometric (the electrical potential of the electrode is sensitive to pH) | 1) Good stability over a wide pH range even at high temperature, high pressure and aggressive environment 2) fast response | No information | Used to develop a pH electrode at high temperature and high pressure | [1] |

4. Results and Conclusions

We found many pH sensitive materials for different detection methods and looked in their physical and/or chemical behaviour, advantages, disadvantages and applications. From this overview we could draw a rough conclusion on which of these materials can be detected by other detection methods.

| pH material (Only number is given, please see section 3 for name of material) | Standard detection method | Possible other detection methods |
|---|---|---|
| 1, 2 | Optical fibre (color change, fluorescence) | Cannot be used for other detection method |
| 3,4 | Magnetoelastic (mass change by shrinking or swelling) | Can be used for Conductimetric (change in electric field), cantilever |
| 5,6 | Conductimetric | Can be used for ISFET, potentiometric |
| 7,8 | ISFET | Can be used for conductimetric, potentiometric and pH image sensor |
| 9 | pH image | Array of ISFETs so can be used for conductimetric, potentiometric |
| 10,11 | Cantilever | Magnetoelastic, conductimetric (swelling changes electric field) |
| 12,13 | Potentiometric | Can be used for conductimetric and ISFET |
| | Glass electrode | Can be used for conductimetric, ISFET |

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