Uses of an Integrated Circuit Novel Sensor for Electrochemical Measurements

V Vignesh¹, S Ananthi^{2*}, A Deepa³ and K Padmanabahn⁴

¹Department of Network Systems & Information Technology, Guindy Campus, University of Madras, Chennai -600 025, India

²Department of Network Systems & Information Technology, Guindy Campus, University of Madras, Chennai -600 025, India

³Research Scholar, Department of Network Systems & Information Technology, Guindy Campus, University of Madras, Chennai -600 025, India

⁴Emeritus Professor (Hony), Alagappa College of Technology, Chennai, India

Received: July 16, 2016; Accepted: July 29, 2016; Published: August 15, 2016

***Corresponding author:** S Ananthi, Associate Professor & Head-in-Charge, Department of Network Systems & Information Technology, Guindy Campus, University of Madras, Chennai -600 025, India. Tel: 044 22202767; E-mail: ananthipradeep84@gmail.com

Abstract

The electrochemical sensors like pH and other concentration cells measure the electrode potential differences across an electrolyte to interface. For example, the pH meter measures the H⁺ ion concentration by finding the voltage difference at the glass electrode to analyte interface. In this paper, a novel chip sensor is introduced in lieu of the usual glass pH and other electrodes for measuring pO₂ or other concentrations. This microelectronic chip is made recently by Plessey Microelectronics for electrophysiological measurements like the ECG. This is of 1 cm square in size with a 0.3 cm thickness and has an integrated circuit built in. It is able to measure very small potentials by direct contact. By a thin layer of dielectric attached to its surface, it somewhat resembles the thin glass surface of a pH electrode. The chip has very high input impedance and an internal amplifier of gain 10 to 100. Thus it can measure voltages without the need for complex circuitry and amplifiers as required for example, with the usual pH electrode. The additional advantage of the above sensor lies in its very fast response compared to the usual glass electrode. Thus, reactions undergoing changes in H⁺ ion concentration can be monitored precisely. A platinum wire reference electrode is used. These sensors are very economical compared to the present chemical electrodes and their amplifiers.

Keywords: Electro Chemical Sensor; Plessey Semiconductors; pH Electrode; Electrolytes; EPIC Sensor

Introduction

Among the various electrochemical measurements, the Hydrogen ion concentration is the most fundamental measurement in chemical analysis. Chemical reactions and many properties of liquids are dependent on this value. Fish life depends for example on the acidity as determined by this concentration in water. It is measured in terms of a number, called the pH value. Various applications demand a continuous and on line measurement of this value. For micro-organisms to thrive, the pH value should be between 6.5 to 7.5. In wastewater treatment, pH value less than 4 and greater than 9 are unsuitable because bio-degradation is annulled. To control this pH, they add HCl and continuous on line monitoring is required. Thus, a novel

compact sensor for pH measurement is a requirement which is not available.

A pH Meter is a device used for measuring the pH, which is either the concentration or the activity of hydrogen ions, of an aqueous solution. The pH is a number which indicates a logarithmic value of the concentration of hydrogen ions. It is actually the minus of the logarithm of the hydrogen ion activity in a solution or, the logarithm of the reciprocal of the hydrogen ion activity in a solution.

$$\text{pH} = \log_{10}(1/\text{H}^+) \quad \dots(1)$$

That gives us a pH of 1 for extremely acidic, pH 7 for neutral, and pH of 14 for extremely alkaline.

When two electrodes are dipped into the test solution, some of the hydrogen ions move toward the outer surface of the glass electrode and replace some of the metal ions inside it, while some of the metal ions move from the glass electrode into the solution. This ion-swapping process is called ion exchange, and it is the key to how a glass electrode works. An electrode potential is also developed if an interface is created by imposing a semipermeable barrier or membrane between two liquid phases so that the membrane allows irreversible transfer of a particular ion.

The pH meter usually has a glass electrode plus a calomel reference electrode, or a combination electrode. The key parts of a pH meter:

- (1) Solution being tested.
- (2) Glass electrode, consisting of
- (3) A thin layer of silica glass containing metal salts, inside which there is a potassium chloride solution
- (4) and an internal electrode
- (5) Made from silver/silver chloride.

The conventional pH meter is shown in (Figure 1). The glass electrode contains a thin glass tube which has at its bottom

a very thin glass membrane. Inside, there is a solution of 0.1N HCl. There is a Silver/Silver Chloride wire extending out of the tube. This is one wire going to the measuring voltmeter. This glass membrane is supposed to be passing H^+ ions from the external measured solution into the inside. This passage of ions of hydrogen carries charge and constitutes a fine current, causing a potential difference to be generated. There should be a return path of this current, which is enabled by the use of a second electrode. This second electrode is also a similar tube with a closed bottom having a fine hole and carrying a porous plug. The tube in its inside contains a solution of saturated KCl. The purpose of this is evidently to reduce the resistance of the path of the ionic current in the path from the solution. The wire used for this second electrode is made highly conducting by using an Hg/HgCl₂ electrode. The wire connection is from mercury to metal contact going to the negative terminal of the voltmeter. There is continuity for both electrodes through the solution whose pH is measured.

The usual pH meter with the Glass Electrode and the Calomel return electrode (Figure 1).

There are variations of this two electrode set up, such as those having a side plug in a combination electrode.

For the measurement of other electrochemical potentials also, electrodes of varying types are in use. The pO_2 electrode called the Clarke Electrode [1] is one such for oxygen concentration measurement in solution. There are other ion selective electrodes also in use. Concentration measurements are based on the Nernst equation for an ion of valence n as

$$\text{Voltage difference } E = -RT/nF \log_{10}(C_{in}/C_{out}) \quad \dots(2)$$

For the pH electrode and the reference electrode, the voltage is

$$E = E_{ref} + 2.303(RT/F) \log_{10} \left(\frac{\text{unknown } H^+}{\text{Internal } H^+} \right) \quad \dots(3)$$

Because of the involvement of the temperature T , the pH electrode voltage varies with the solution temperature as $E = E_0 - kT \cdot \text{pH}$. At 20°C, if it is -58mV per pH, at 50°C, it is -64.1 mV per pH.

R = molar gas constant 8.314 J/ mol/ °K, F : Faraday constant = 96485 C/ mol.

Figure 1: The usual pH meter with the Glass Electrode and the Calomel return electrode.

The value of RT/F for H^+ ion is 0.061 or 61 mV at room temperature. This translates to 61mV per unit pH change.

The C denotes outer and inner concentrations. In a pH meter with Glass electrode as shown, the inside is having plenty of ions due to the saturated buffer solution and so, the voltage depends mainly on the outside liquid concentration C_{out} of the respective ion, viz, the H^+ ion.

The actual readings of a pH probe are subject to errors and the values read are not exactly as per the equations above. Hence, all instruments are to be calibrated with known pH buffer solutions.

First, Nobel-Prize winning German chemist Fritz Haber (1868–1934) and his student Zygmunt Klemensiewicz (1886–1963) developed the glass electrode idea in 1909 [2, 3]. American chemist Arnold Beckman (1900–2004) figured out how to hook up a glass electrode to an amplifier and voltmeter to make a much more sensitive instrument [4].

The important facts about these pH and other ion selective electrodes are:

1. The Electrode set is made of slender glass and more specifically, the tip is of a very fine glass of special type Borosilicate. The same needs delicate handling.
2. Two electrodes are needed; both are slender glass pieces.
3. The output impedance, even with the use of saturated buffer and mercury contacts in the main and return electrodes, is extremely high, of value 10-100 Mega-ohms. That means the electrodes are mainly insulating.
4. The size of the glass electrode along with its internal solution and wires is such that the unit is not a compact or miniature one.
5. The electrode has to be stored in liquid solution always, as otherwise, the tip will be spoiled.
6. Because of its high output impedance, an electrometer amplifier is needed, which is a special valve component. Recently, special differential MOSFET transistors are used to cater to the high output impedance.
7. The voltage generated per pH is about 60 mV and requires further amplification.
8. The response time of the pH probe is rather slow because of the use of a capacitor at the input of the amplifier and the series high output impedance. The time constant is about a minute. This is fairly large when sudden changes in concentrations in solution for reactions are measured.
9. If the glass membrane or the diaphragm is dirty, e.g. oil, fat, paint, dirt, then the voltage developed fluctuates widely.

Development of a Novel Integrated Sensor Micro-electrode

Plessey Inc., U.S.A. has recently [5] developed a sensor electrode, especially meant for ECG of human subjects as an integrated electrode cum amplifier, having an extremely high input impedance, a good gain and very small size of just 1cm square and 0.4 cm thick.

Epic Sensor

Plessey Semiconductors Electric Potential Integrated Circuit (EPIC) product line targets a range of applications. The PS25251 is an ultra high impedance solid state sensor. The resolution available is as good as or better than conventional electrodes. The device uses active feedback techniques to both lower the effective input capacitance of the sensing element (C_{in}) and boost the input resistance (R_{in}). These techniques are used to realise a sensor with a frequency response suitable for such application. Its important features are listed below;

- Ultra high input resistance, typically 20GΩ.
- Dry-contact capacitive coupling.
- Input capacitance as low as 15pF.
- Lower -3dB point typically 200 mHz.
- Upper -3dB point typically 10 kHz.
- Operates with bipolar power supply from $\pm 2.4V$ to $\pm 5.5V$.
- Sensors supplied in a custom package with exposed pins for surface mount assembly.

In this paper, the deployment of this integrated circuit sensor is described for electrochemical measurements and results given.

As far as the history of the development of the pH or similar electrodes goes, in those days, they were not aware of techniques presently used in fabrication of integrated circuits. The idea of using the Plessey microelectrode EPIC™ sensor is based on the following considerations.

- The EPIC sensor has a glass-ceramic outer enclosure and houses the tiny integrated circuit high input impedance amplifier within. Thus, the sensor's outer encapsulation is very similar to the glass membrane of the usual pH or other electrodes for ion transport.
- The pH electrode development was done by the Chemists of those days, and they imagined the flow of hydrogen ions through the glass membrane and provided for its free flow, without any generated intervening potentials, by using saturated buffer solution for the main electrode and the use of Calomel solution of neutral strength (neither acid nor base) and the mercury contact for good conductivity. In the present EPIC sensor, these requirements are unnecessary because of the immediately located integrated high input impedance amplifier within it. Figure 2 shows the EPIC sensor and its internal electronics.

The special Plessey EPIC ECG microchip electrode and Internal Chip Circuit in figure 2.

There was a need for a reference electrode in the usual pH meter. This is not necessary in this case because the EPIC sensor just needs the earth reference and no return current flows because of the extremely high input impedance of the sensor. In figure 3, a comparison of the two measuring methods, the conventional and this novel sensor based, is shown.

As per the diagram shown below (Figure 3), the difference in the concentrations of Hydrogen ions across each interface, the main and the reference electrodes, a difference voltage is sensed by the meter. A salt bridge connection was added because the small currents have to return back to the solution [6]. This was improvised by the early workers through a similar electrode made of Calomel solution. This is to avoid the generation of liquid potentials at the reference electrode.

The use of EPIC sensor for a pH meter as improvised by the authors is as follows. The solution under examination is just kept in contact on its outer surface by the EPIC sensor itself. A

Figure 2a: Shows the special Plessey EPIC ECG microchip electrode.

Figure 2b: Showing the internal chip circuit of the sensor.

thermocole float is usable so that when the liquid changes in level, the sensor surface will always maintain contact with the liquid surface.

The need for the second electrode is dispensed with. To avoid electrochemical voltages with wires, a Platinum wire is used for the return electrode, which is connected to the Ground pin of the EPIC sensor.

The comparison of the usual pH Glass electrode-Calomel Electrode type and the EPIC sensor-Platinum wire type in (Figure 3).

As per equation (3), the Unknown H^+ for the EPIC sensor is dependant on its internal semiconductor structure and the metal film tracks. Therefore, the actual voltage picked up will be not just the solution pH alone.

$$E = E_{ref} + 2.303(RT/F) \{ \log (H^+_{semiconductor}) - \log (H^+_{Solution}) \} \quad [4]$$

So, the actual voltage sensed is different by the value of $2.303(RT/F) \{ \log (H^+_{semiconductor}) \}$ which is a constant for a particular EPIC sensor chip. The variations of voltage are only due to the second term, which is the required pH. So, absolute voltages from the sensor are not the same as with the Glass electrode. In any case, a calibration is always required and herein, this calibration is done similarly and hence the results of pH readings shown on a meter attached to the sensor electronics will not vary (Figure 4).

The sensor has a gain of 10. Thus, voltages are available sufficiently large to be shown on a digital voltmeter. The variation with pH over the range 4 to 9 is shown in the graph below (Figure 5).

The principle of pH measurement with EPIC Sensor in figure 4.

Experimental Results

Using the set up with an amplifier of gain 10, measurements were made with acid, alkali of various concentrations as well as pH buffer solutions of value 4, 6.8 and 9.2.

The results were repeatable. The response time was measured by changing the pH of the solution by adding a dilute acid. The graph of the response is shown in figure 5. This indicates a faster response in milliseconds rather than the several seconds as in the usual pH meter.

Figure 4: The principle of pH measurement with EPIC Sensor.

Figure 5: The response time is about 0.3 seconds (Time base 0.2s per division).b) Volts vs. pH.

The response time is about 0.3 seconds (Time base 0.2s per division) and plotted Graph between Volts vs. pH in figure 5.

Accuracy

The accuracy of any pH measurement depends on the amplifier mainly. The variations with temperature are usually compensated by extra circuitry. In our work, a microcontroller (Aurdino board) was used to digitise the output of the sensor, display it on an LCD display.

Temperature compensation as per the Nernst equation is done by the program on the embedded controller. Thus, the meter is rendered intelligent. The Aurdino board is a very compact 4cm x 2 cm p.c.b. and provides support for extended software and adding several peripherals. Its communication port is also useful for making a pH transmitter as needed in chemical industry.

Response time to pH changes: In continuous control of pH as required for wastewater treatment etc., the time constant of the sensor is of importance. The Glass electrode pH meters are having a time constant in the range 50-60 seconds.

Other pH sensors

The LanceFET probe contains Sentron's non-glass ISFET (Ion Sensitive Field Effect Transistor) pH sensor. This sensing component is Sentron's proprietary design and has been improved continuously over the past 15 years. They claim 5-6 seconds response time [7, 8].

The Ion-selective Field Effect Transistor (ISFET) pH electrode provides a stable pH measurement. Its rate of response can be ten times faster than glass electrodes.

Conclusion

As a dynamic and fast acting pH probe, the EPIC sensor serves ideally for most industrial applications. Its small footprint, low cost and ease of use as well as its rigidity are important aspects in any application. There are also other ISFET based sensor pH meters but the present sensor is extremely small in size and comes with built in amplifier so that the output can be easily interfaced to any electronics. The sensor is applicable for wastewater treatment for pH control [9] ideally since it can be left in such an environment as well.

Reference

1. Leland C Clark JR, Richard Wolf, Donald Granger, Zena Taylor. Continuous recording of blood oxygen tensions by polarography. J Appl Physiol. 1953;6(3):189-193. PMID:13096460.

2. Wikipedia contributors, Fritz Haber Wikipedia, The Free Encyclopedia. cited 2015 Dec 15: https://en.wikipedia.org/w/index.php?title=Fritz_Haber&oldid=704308501
3. JR Roman Jakub Jakimowicz, Zasady taternictwa, Volume 2 of Wydawnictwa Sekcji Turystycznej Polskiego Towarzystwa Tatrzańskiego, nakł. Sekcji Turystycznej Towarzystwa Tatrzańskiego, 1913.
4. Robert D, Simoni Robert L, Hill Martha Vaughan, Herbert Tabor A. Classic Instrument: The Beckman DU Spectrophotometer and Its Inventor, Arnold O. Beckman. The Journal of Biological Chemistry. 2003;278(49):79-81.
5. ECG using wrist-mounted EPIC sensors. Plessey Semiconductors, Application Note #291465, 2010. Date of retrieval. 8.1.2013; Available at: <http://www.plesseysemiconductors.com>
6. Cole-Parmer, Electrochemistry, Process & Control - . 2015.12.15; Available From: www.coleparmer.com/TechLibraryArticle/560
7. Sentron Europe BV, Steel tipped ISFET pH probe. 2015.12.15; Available at: www.sentron.nl/index.php/download_file/93/150/
8. Emerson Electric Co, pH Electrodes - TUPHFET™ Non-glass Submersion/Insertion pH Sensor -- Model TF39, 2015.12.15; Available at: <http://www2.emersonprocess.com/en-us/brands/rosemountanalytical/liquid/sensors/ph/tuph/tf396/pages/index.aspx>
9. Alwan GM. pH-Control Problems of Wastewater Treatment Plants. Al-Khwarizmi Engineering Journal. 2008;4(2):37- 45.