AN-1852 Designing With pH Electrodes

ABSTRACT

A pH electrode measures hydrogen ion (H+) activity and produces an electrical potential or voltage. The operation of the pH electrode is based on the principle that an electric potential develops when two liquids of different pH come into contact at opposite sides of a thin glass membrane. This was originally discovered in 1906 by Max Cremer [1]. His discovery laid the foundation for Fritz Haber and Zygmunt Klemensiewicz, who published their findings in 1909, to create the first glass electrode that measured hydrogen activity [2]. Today, modern pH electrodes use the same principles to measure pH in a variety of applications including water treatment, chemical processing, medical instrumentation, and environmental test systems.

Contents

List of Figures

1   Introduction

The modern pH electrode is a combination electrode composed of two main parts: a glass electrode and a reference electrode as shown in Figure 1. pH is determined essentially by measuring the voltage difference between these two electrodes. At the tip of the electrode is the thin membrane that is a specific type of glass that is capable of ion exchange. It is this element that senses the hydrogen ion concentration of the test solution. The reference electrode potential is constant and is produced by the reference electrode internal element in contact with the reference-fill solution that is kept at a pH of seven.
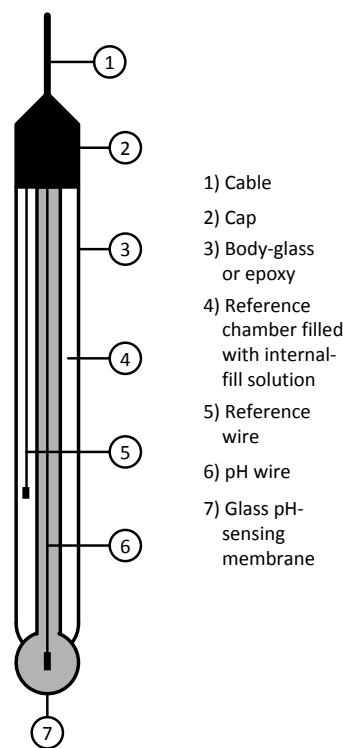

1) Cable

2) Cap

3) Body-glass
   or epoxy

4) Reference
   chamber filled
   with internal-
   fill solution

5) Reference
   wire

6) pH wire

7) Glass pH-
   sensing
   membrane

Figure 1. Typical pH Glass Electrode

1.1   pH Electrode Characteristics

When designing with a pH electrode, as with any sensor, it is important to understand the sensor characteristics and how they affect a specific application. These characteristics include whether the sensor is active or passive, unipolar or bipolar, and whether it has a voltage or current output. Sensor sensitivity, linearity, full scale range, and source impedance should also be considered.

The pH electrode is a passive sensor, which means no excitation source (voltage or current) is required. Because the electrode's output can swing above and below the reference point, it is classified as a bipolar sensor. It produces a voltage output that is linearly dependent upon the pH of the solution being measured.

The source impedance of a pH electrode is very high because the thin glass bulb has a large resistance that is typically in the range of 10 MΩ to 1000 MΩ. This means that the electrode can only be monitored by a high-impedance measuring device.

The transfer function of the pH electrode is:

$$pH\,(X) = pH\,(S) + \frac{(E_S - E_X)\,F}{RT\,\ln(10)}$$

(1)

where

- $pH(X)$ = pH of unknown solution(X)
- $pH(S)$ = pH of standard solution = 7
- E_S = Electric potential at reference or standard electrode
- E_X = Electric potential at pH-measuring electrode
- F is the Faraday constant = 9.6485309×10^4 C mol^{-1},
- R is the universal gas constant = 8.314510 J K^{-1} mol^{-1}
- T is the temperature in Kelvin

The transfer function in Figure 2 and Figure 3 shows that as the pH of the solution increases, the voltage produced by the pH-measuring electrode decreases.
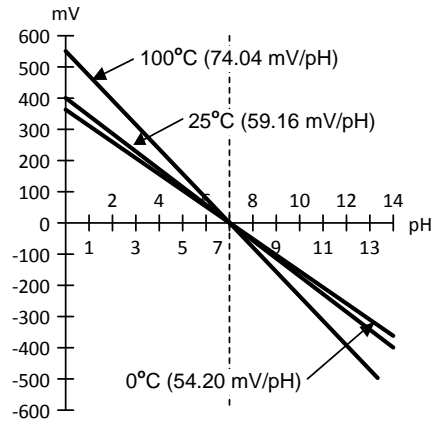
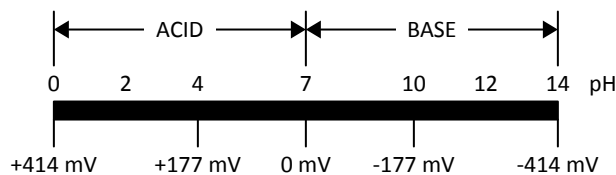

Figure 2. pH-Electrode Transfer Function

Figure 3. pH Scale

It is important to note that a pH electrode's sensitivity varies over temperature. Looking at the pH-electrode transfer function shows that the sensitivity linearly increases with temperature according to Equation 2:

$$\frac{RT\,\ln(10)}{F} \quad \text{or} \quad 0.000198T \text{ V/pH}$$

(2)

This results in a sensor output full-scale range that is dependent on the temperature. For example, at 25°C, electrode sensitivity is 59.16 mV/pH and the output of the electrode will swing from -7pH x -59.16 mV/pH = +414.12 mV (pH 0 strong acid) to +7 pH x -59.16 mV/pH = -414.12 mV (pH 14 strong base). However, if the measured solution temperature is increased to 100°C, the output will swing from -7pH x -74.04 mV/pH = +518.29 mV down to +7pH x -74.04 mV/pH = -518.29 mV. Due to this behavior, it is critical to know the temperature of the solution being measured and compensate the measurement accordingly.

An ideal electrode at 25°C will produce 0 mV when placed in a solution with a pH of seven. Of course, real-world electrodes are not ideal and will have an actual reading that varies from 0 mV. This variation is called the electrode's off set error. As stated previously, the sensitivity of an ideal electrode at 25°C is 59.16 mV per pH unit. Any variation from this ideal value is specified as the electrode's span error. These errors will need to be accounted for through calibration if high system accuracy is required.

1.2   An Optimum pH-Electrode Circuit

The important sensor characteristics described need to be accounted for in order to design a circuit that will condition the sensor signal so that it can be faithfully utilized by other components (such as an ADC, microcontroller, and so forth) along the signal path. First, because the pH electrode produces a bipolar signal and most applications operate on a single supply, the signal will have to be level shifted. Second, due to the high impedance of the electrode, a high-input impedance buffer will be required. Finally, the temperature of the measured solution must be known in order to compensate for the electrode's sensitivity variation over temperature.

Figure 4. pH-Electrode Circuit

The circuit in Figure 4 solves all three design challenges. Amplifier U1 off sets the pH electrode by 512 mV. This is achieved by using TI's LM4140A-1.0 precision micro-power low-dropout voltage reference that produces an accurate 1.024 V. That voltage is divided in half to equal 512 mV by the 10 kΩ resistor divider. The output of amplifier U1, that is set up in a unity-gain configuration, biases the reference electrode of the pH electrode with the same voltage, 512 mV, at low impedance. The pH-measuring electrode produces a voltage that rides on top of this 512 mV bias voltage. In effect, the circuit shifts the bipolar pH-electrode signal to a unipolar signal for use in a single-supply system.

The second amplifier U2 is set up in a unity-gain configuration and buffers the output of the pH electrode. Again, a high-input impedance buffer between the pH electrode and the measurement instrument allows the circuit to interface with a greater variety of measurement instruments including those with lower input impedance. In most applications, the output voltage of the pH electrode is high enough to use without additional amplification. If amplification is required, this circuit can easily be modified by adding gain resistors to U2.

TI's LM35 precision centigrade temperature sensor is added to the circuit to measure the temperature of the solution so that adjustments are made for the variance in sensitivity due to temperature. This will result in an accurate temperature-corrected pH measurement.

The circuit results in the transfer function:

$$V_{OUT} = VpH + 512 \text{ mV} \tag{3}$$

For example, if room temperature (25°C) household ammonia (NH_3) that has a typical pH of 11.5 were measured, the voltage produced by the pH electrode would be -266 mV resulting in an output voltage of 246 mV.

1.3   Amplifier Selection

The specific design challenges of the pH electrode impose the need to select an amplifier that does not degrade the overall system performance. It is best to start with an understanding of what amplifier parameters contribute most to the voltage error in a pH-electrode application. The most significant parameter to consider is the amplifier's input-bias current. This is because even a small input-bias current can produce a large voltage error when injected into the very high impedance of a pH electrode.

That makes TI's LMP7721 PowerWise™ op amp, which is the industry's lowest assured input-bias-current precision amplifier, a natural fit. The latest patent-pending technology of input-bias-current cancellation amplifier circuitry achieves a remarkably low input-bias-current of only 3 fA. This technology also maintains ensured specifications of 20 fA at room temperature and 900 fA at 85°C over the entire input common-mode voltage range of the amplifier.

With such a low input-bias current, any PCB parasitic-leakage current that reaches the input pins of the device could have a significant adverse effect on system accuracy. The LMP7721 amplifier minimizes this effect with a special pinout that isolates the amplifier's input from the power supply and output pins. As Figure 5 shows, this unique pinout makes it easy to guard the LMP7721 amplifier's input and achieve optimal system performance.
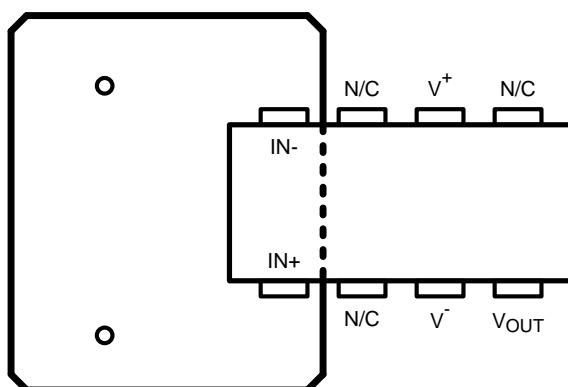

Figure 5. Circuit Board Guard Layout

Other amplifier parameters that need to be considered are amplifier input-offset voltage and input-offset drift. In the pH-electrode circuit described above, any amplifier offset voltage is added to the pH sensor offset twofold. The level-shifting amplifier (U1) adds offset directly to the pH-reference electrode whose main function is to stay constant. On top of that, the buffer amplifier (U2) adds its individual offset voltage to the output of the pH-measuring electrode. These offsets will have a greater impact on the system if it is decided that amplifier gain is required. With low DC-offset voltage (150 µV maximum at 25°C) and low off set-voltage drift (1.5 µV/°C), the LMP7721 amplifier allows a designer to achieve the most accurate pH measurements.

As part of TI's PowerWise products, the LMP7721 op amp provides the remarkably wide gain bandwidth product of 17 MHz while consuming only 1.3 mA of current. This wide gain bandwidth along with the high open loop gain of 120 dB enables accurate signal conditioning. With these specifications, the LMP7721 op amp has the performance to excel in pH-electrode circuits.

The pH electrode is a temperature-dependent bipolar sensor that has a very large source impedance. These design challenges are handled with level shifting and temperature compensation in a single-supply pH-electrode circuit. When deciding on an amplifier to use in this circuit, it is important to understand that using an amplifier with a low bias current is of utmost importance. Selecting an amplifier with ultra-low bias current such as TI's PowerWise LMP7721 3 fA input-bias-current precision amplifier is the best choice.

1.4 References

1. Cremer M (1906): Z. Biol, 47, 562
2. Haber F and Z Klemensiewicz (1909): Z. Physik. Chem., 67, 385

IMPORTANT NOTICE

Texas Instruments Incorporated and its subsidiaries (TI) reserve the right to make corrections, enhancements, improvements and other changes to its semiconductor products and services per JESD46, latest issue, and to discontinue any product or service per JESD48, latest issue. Buyers should obtain the latest relevant information before placing orders and should verify that such information is current and complete. All semiconductor products (also referred to herein as "components") are sold subject to TI's terms and conditions of sale supplied at the time of order acknowledgment.

TI warrants performance of its components to the specifications applicable at the time of sale, in accordance with the warranty in TI's terms and conditions of sale of semiconductor products. Testing and other quality control techniques are used to the extent TI deems necessary to support this warranty. Except where mandated by applicable law, testing of all parameters of each component is not necessarily performed.

TI assumes no liability for applications assistance or the design of Buyers' products. Buyers are responsible for their products and applications using TI components. To minimize the risks associated with Buyers' products and applications, Buyers should provide adequate design and operating safeguards.

TI does not warrant or represent that any license, either express or implied, is granted under any patent right, copyright, mask work right, or other intellectual property right relating to any combination, machine, or process in which TI components or services are used. Information published by TI regarding third-party products or services does not constitute a license to use such products or services or a warranty or endorsement thereof. Use of such information may require a license from a third party under the patents or other intellectual property of the third party, or a license from TI under the patents or other intellectual property of TI.

Reproduction of significant portions of TI information in TI data books or data sheets is permissible only if reproduction is without alteration and is accompanied by all associated warranties, conditions, limitations, and notices. TI is not responsible or liable for such altered documentation. Information of third parties may be subject to additional restrictions.

Resale of TI components or services with statements different from or beyond the parameters stated by TI for that component or service voids all express and any implied warranties for the associated TI component or service and is an unfair and deceptive business practice. TI is not responsible or liable for any such statements.

Buyer acknowledges and agrees that it is solely responsible for compliance with all legal, regulatory and safety-related requirements concerning its products, and any use of TI components in its applications, notwithstanding any applications-related information or support that may be provided by TI. Buyer represents and agrees that it has all the necessary expertise to create and implement safeguards which anticipate dangerous consequences of failures, monitor failures and their consequences, lessen the likelihood of failures that might cause harm and take appropriate remedial actions. Buyer will fully indemnify TI and its representatives against any damages arising out of the use of any TI components in safety-critical applications.

In some cases, TI components may be promoted specifically to facilitate safety-related applications. With such components, TI's goal is to help enable customers to design and create their own end-product solutions that meet applicable functional safety standards and requirements. Nonetheless, such components are subject to these terms.

No TI components are authorized for use in FDA Class III (or similar life-critical medical equipment) unless authorized officers of the parties have executed a special agreement specifically governing such use.

Only those TI components which TI has specifically designated as military grade or "enhanced plastic" are designed and intended for use in military/aerospace applications or environments. Buyer acknowledges and agrees that any military or aerospace use of TI components which have *not* been so designated is solely at the Buyer's risk, and that Buyer is solely responsible for compliance with all legal and regulatory requirements in connection with such use.

TI has specifically designated certain components as meeting ISO/TS16949 requirements, mainly for automotive use. In any case of use of non-designated products, TI will not be responsible for any failure to meet ISO/TS16949.

Products		Applications	
Audio	www.ti.com/audio	Automotive and Transportation	www.ti.com/automotive
Amplifiers	amplifier.ti.com	Communications and Telecom	www.ti.com/communications
Data Converters	dataconverter.ti.com	Computers and Peripherals	www.ti.com/computers
DLP® Products	www.dlp.com	Consumer Electronics	www.ti.com/consumer-apps
DSP	dsp.ti.com	Energy and Lighting	www.ti.com/energy
Clocks and Timers	www.ti.com/clocks	Industrial	www.ti.com/industrial
Interface	interface.ti.com	Medical	www.ti.com/medical
Logic	logic.ti.com	Security	www.ti.com/security
Power Mgmt	power.ti.com	Space, Avionics and Defense	www.ti.com/space-avionics-defense
Microcontrollers	microcontroller.ti.com	Video and Imaging	www.ti.com/video
RFID	www.ti-rfid.com		
OMAP Applications Processors	www.ti.com/omap	**TI E2E Community**	e2e.ti.com
Wireless Connectivity	www.ti.com/wirelessconnectivity		