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Designing with pH Electrodes

Application Note AN-1852

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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 which 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.

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 which 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 which is kept at a pH of seven.

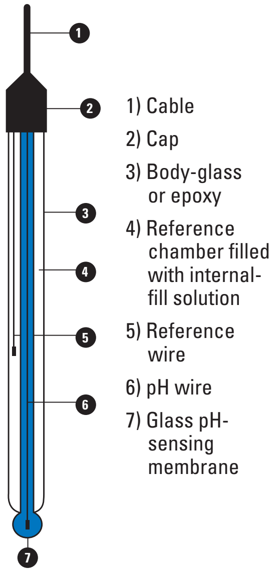

Figure 1. Typical pH Glass Electrode

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 which 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 which 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:

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

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

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

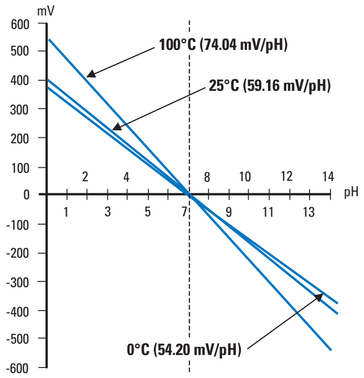

Figure 2. pH-Electrode Transfer Function

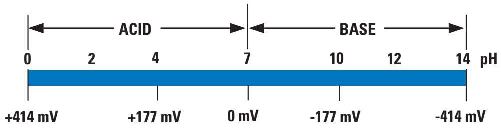

Figure 3. pH Scale

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 the following equation:

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

This results in a sensor output full-scale range which 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 which varies from 0 mV. This variation is called the electrode's offset 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.

An Optimum pH-Electrode Circuit

The important sensor characteristics described need to be accounted for in order to design a circuit which will condition the sensor signal so that it can be faithfully utilized by other components (such as an ADC, microcontroller, etc.) 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.

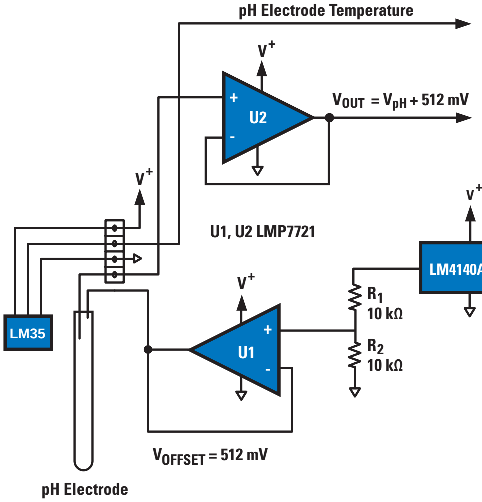

Figure 4. pH-Electrode Circuit

The circuit in *Figure 4* solves all three design challenges. Amplifier U1 offsets the pH electrode by 512 mV. This is achieved by using National's LM4140A-1.0 precision micro-power low-dropout voltage reference that produces an accurate 1.024V. That voltage is divided in half to equal 512 mV by the 10 kΩ resistor divider. The output of amplifier U1, which 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 will produce a voltage which 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.

National'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:

$$V_{OUT} = VpH + 512\ mV$$

For example, if room temperature (25°C) household ammonia (NH_3) which 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.

Amplifier Selection

The specific design challenges of the pH electrode impose the need to select an amplifier which 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 National's LMP7721 PowerWise® op amp, which is the industry's lowest guaranteed 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 guaranteed 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 which 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.

Other amplifier parameters which 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 offset-voltage drift (1.5 µV/°C), the LMP7721 amplifier allows a designer to achieve the most accurate pH measurements.

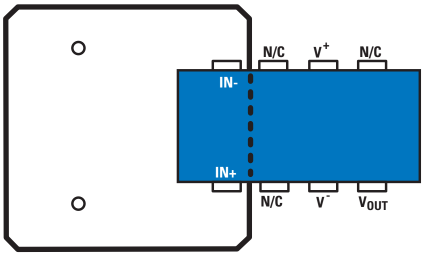

Figure 5. Circuit Board Guard Layout

As part of National'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 which 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 National's PowerWise LMP7721 3 fA input-bias-current precision amplifier is the best choice. ■

To learn more about amplifiers, visit:
national.com/amplifiers

References:

[1] *Cremer M (1906): Z. Biol, 47, 562*

[2] *Haber F and Z Klemensiewicz (1909): Z. Physik. Chem., 67, 385*

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