79th Annual Instrumentation and Automation Symposium
For the Process Industries
October 20-22, College Station, Texas

pH Measurement Best Practices

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Abstract

*p*H measurement has the greatest sensitivity and rangeability by far of any ion composition measurement. However, there are many challenges in terms of the installed accuracy and life expectancy. Many electrode designs have severe limitations when used in an industrial plant that could dramatically increase errors and failure rate. Here we provide guidance on the effect of process conditions and electrode designs, and offer best practices to take advantages of the advances in electrode technology, calibration, installation designs, and online diagnostics to get the best performance and reliability.

Keywords: measurement electrodes, middle signal selectrion, reference electrodes

A Dose of Reality (*Advanced pH Measurement and Control Fourth Edition,* ISA 2024)

The incredible sensitivity and rangeability of the *p*H measurement is based on a series of assumptions, most of which are not sufficiently explained in the literature. Manufacturers have been doing a better job at noting some considerations, especially as they develop new electrode features that can address a particular application problem. In this section, equations are presented that reveal underlying assumptions to help the user cut through the hype. With *p*H electrodes more than any other sensor, there is a need to "keep it real."The accuracy and speed of response of the pH measurement depends upon the condition of a hydrated gel layer on the surface of the glass electrode that is only 10^{-4} mm thick and the condition of a junction of the reference electrode illustrated in Figure 1 for a combination electrode that provides a physical contact between its internal electrolyte and the process solution. The need for the fragile gel layer and the process junction of the reference to be structurally consistent, clean, and free from contamination has profound implications for the proper selection, calibration, and maintenance of *p*H measurements. The fact that *p*H sensors perform as well as they do despite exposure to a wide variety of chemicals, temperatures, and pressures is truly remarkable and testimony to the ingenuity of electrode designs.
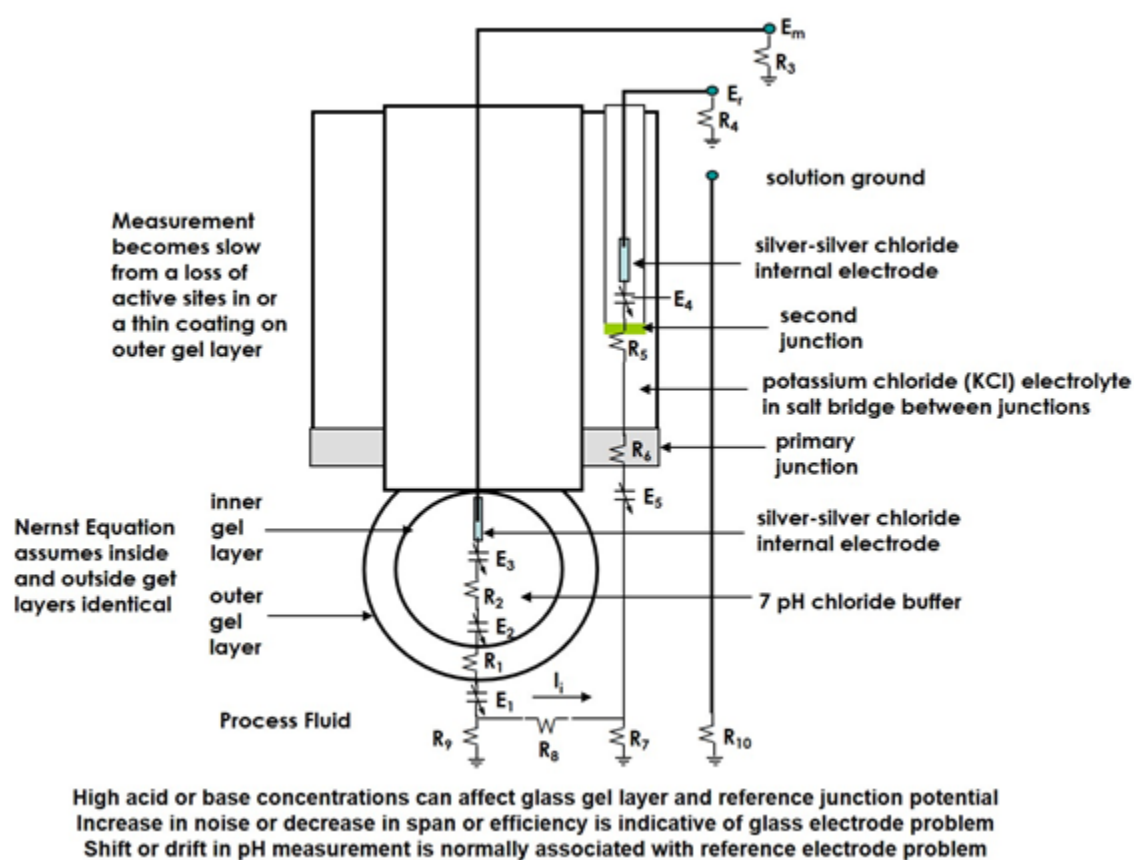
Figure 1. Equivalent Electrical Schematic of a Double Junction Combination Electrode

The actual sensing of *p*H is accomplished by having a *p*H -sensitive glass in contact with the internal fill, a 7pH buffer, and the external solution. The *p*H sensitive glass develops potentials per Equations 1a and 1d, which are Nernst equations, by the hydrogen ion (proton) exchange between hydronium ions in aqueous solutions and in the hydrated gel layer of the glass. The migration of hydronium ions through the boundary layer that surrounds the surface takes several seconds even under the best of conditions, but once the hydronium ions are in very close proximity to the surface, protons jump from the hydronium ions and become associated with water molecules on the surface. There is no migration of hydronium ions intact into the surface but rather a proton transfer that occurs for aqueous and non-aqueous solutions. As protons move into one surface from a greater dissociation of hydrogen ions, they move out of the surface on the other side of the glass. Lithium and sodium ions in the dry interior of the glass provide the electrical continuity between the internal and external hydrated gel layers. Thus, current flow through the glass consists of the conduction of single charged positive ions (cations). The potential developed is proportional to the difference in logarithms of the activity of hydronium ions in solution and in the gel layer on each side of the glass membrane. If the gel layers have an equal number of sites for proton exchange, the constants K_{g1} and K_{g2} will be equal and Equations 1c and 1e can be combined to yield Equation 1f. If all the original lithium or sodium ions at these sites in the gel are also replaced by protons, the activities ag1 and ag2 are equal, which yields Equation 1g. By use of the definition of *p*H, the logarithms of hydrogen activity can be converted to *p*H, which yields Equation 1h, where the difference in potentials is proportional to the difference in *p*H. Also, because the internal fill has a hydrogen activity that corresponds to 7 *p*H, the potential difference becomes Equation 1i, which

is the equation that is typically shown in the literature. Examination of this simplified equation for the ideal *p***H** measurement electrode yields the following conclusions:

(1) At 25°C, the output decreases from +480 mv at 0 *p***H** to −480 mv at 14 *p***H**.
(2) The output is 0 mv at 7 *p***H**.
(3) There is no effect of temperature changes on the electrode output at 7 *p***H**.
(4) At 25°C, the output changes by 59 mv per *p***H** unit.

The general Nernst Equation:

$$E_1 = E_0 + \frac{R*(T+273.16)}{F} \tag{1a}$$

For the exterior surface of the pH glass electrode:

$$E_1 = K_{g1} + 0.1984*(T + 273.16)*\log \left[\frac{a_1}{a_{g1}} \right] \tag{1b}$$

$$E_1 = K_{g1} + 0.1984*(T+ 273.16)*[\log (a_1) - \log (a_{g1})] \tag{1c}$$

For the interior surface of the pH glass electrode:

$$E_2 = K_{g2} + 0.1984*(T+ 273.16)*\log \left[\frac{a_2}{a_{g2}} \right] \tag{1d}$$

$$E_2 = K_{g2} + 0.1984*(T + 273.16)*[\log (a_2) - \log (a_{g2})] \tag{1e}$$

If $K_{g1} = K_{g2}$, then:

$$E_1 - E_2 = 0.1984*(T + 273.16)*[\log (a_1) - \log (a_{g1}) + \log (a_{g2}) - \log (a_2)] \tag{1f}$$

If also $a_{g1} = a_{g2}$, then:

$$E_1 - E_2 = 0.1984*(T + 273.16)*[\log (a_1) - \log (a_2)] \tag{1g}$$

Because $pH_1 = - \log (a_1)$ for external process and $pH_2 = - \log (a_2)$ for internal electrolyte:

$$E_1 - E_2 = 0.1984*(T + 273.16)*(pH_2 - pH_1) \tag{1h}$$

Because the internal buffer of the glass electrode is 7 pH:

$$E_1 - E_2 = 0.1984*(T + 273.16)*(7 - pH_1) \tag{1i}$$

Where:

a_1 = activity of hydrogen ions in external process fluid (normality)
a_2 = activity of hydrogen ions in internal fill fluid (normality)
a_{g1} = activity of hydrogen ions in outer gel surface layer (normality)
a_{g2} = activity of hydrogen ions in inner gel surface layer (normality)
E_o = potential developed at standard conditions (millivolts)
E_1 = potential developed at external glass surface (millivolts)
E_2 = potential developed at internal glass surface (millivolts)
F = Faraday constant (degrees K per mole)
K_{g1} = constant for potential for outer gel surfaces layer (millivolts)
K_{g2} = constant for potential for inner gel surfaces layer (millivolts)
pH_1 = pH of external solution
PH_2 = pH of internal solution (typically 7pH)
R = universal gas constant (Joules per deg K and moles)
T = solution temperature (degrees C)

Water molecules in the glass surface are essential for the proton transfer to occur. Non-hygroscopic glasses such as Pyrex and quartz show no pH response. Glasses that can absorb water but have lost their gel layer from contact with non-aqueous and highly acidic or basic solutions or from long term exposure to air will lose their pH response. It takes about 2 hours of immersion in water to replenish a completely dehydrated gel layer.

Instead of a sharp transition between the gel and dry layers, there is continuous decrease in the number of hydronium ions and an increase in the number of lithium or sodium ions from the surface to the interior of glass. As the electrode ages, the outside surface is stripped away and the gel layer penetrates deeper into the glass. Eventually there is a complete breakdown of the silicon oxygen network that forms the glass matrix. For ideal conditions, (25 degrees C and zero ionic strength solutions between 6 and 8 *pH*), a satisfactory glass response should last 2 to 3 years. Most of the variation in life expectancy for these conditions is associated with the manufacturing tolerances with the greatest variability shown for manual glass blowing and assembly. Chemical attack from strong alkaline and acidic solutions, high temperatures, and non-aqueous solutions greatly accelerates corrosion and depletion of the gel layer. The decrease in the electrode efficiency (slope of the millivolt versus pH plot) during the aging process is usually quite moderate (<5%) until a complete loss of the response (zero efficiency and slope) occurs.

The following equation for the input potential (E_i) seen by *pH* transmitters reveals many of the more notable extraneous potentials that cause errors in the measurements

$$E_i = E_1 - E_2 - E_3 + E_4 + E_5 - I_i * (R_1 + R_2 + R_5 + R_6 + R_8) \qquad (1j)$$

Normalizing Equation 1i for 25°C so that the slope is 59.1 mv per *pH* (0.1984 * 298):

$$E_1 - E_2 = 59 * \frac{(T + 273)}{298} * (7.0 - pH_1) \qquad (1k)$$

Lumping all the extraneous voltage offsets into one bias voltage:

$$E_{bias} = -\,E_3 + E_4 + E_5 - I_i * (R_1 + R_2 + R_5 + R_6 + R_8) \qquad (1l)$$

Substituting (1k) and (1l) into (1j), and solving for *p***H**:

$$pH_1 = 7.0 \; - \; \frac{E_i - E_{bias}}{[59.1 * (T + 273) / 298]} \qquad (1m)$$

Using digital meter calibration factors with Nernst temperature compensation:

$$pH_1 = \; pH_{iso} - \; \frac{E_i - E_{std}}{[(S_{eff} / 100\%) * S_{slope} * (T + 273) / 298]} \qquad (1mx)$$

Adding solution temperature compensation:

$$pH_{25\,^oC} = pH_1 + K_1 * (T - T_{ref}) \; + \; K_2 * (T - T_{ref})^2 \qquad (1n)$$

Adding digital transmitter calibration factors to transmit a controlled variable in percent:

$$CV_\% = \frac{pH_{25^oC} - pH_{0\%}}{pH_{100\%} - pH_{0\%}} * 100\% \qquad (1o)$$

Some digital transmitters have a *p***H** span adjustment defined as follows:

$$pH_{span} = pH_{100\%} - pH_{0\%} \qquad (1p)$$

where
  $CV_\%$ = controlled variable for *p***H** controller in percentage of scale (%)
  E_i = potential that is the input seen by the *p***H** transmitter (millivolts)
  E_1 = potential developed at the external glass surface (millivolts)
  E_2 = potential developed at the internal glass surface (millivolts)
  E_3 = half-cell potential at the measurement internal electrode (millivolts)
  E_4 = half-cell potential at the reference internal electrode (millivolts)
  E_5 = liquid junction (diffusion) potential of the reference electrode (millivolts)
  E_{bias} = asymmetry and offset voltages lumped as one bias voltage (millivolts)
  E_{std} = electrode standardization potential (millivolts)
  K_1 = solution temperature compensation first-order correction factor (*p***H** per ^oC)
  K_2 = solution temperature compensation second-order correction factor (*p***H** per ^oC)
  I_i = input leakage current of the preamplifier (milliamps)
  pH_{iso} = isopotential point (point of zero temperature effect) (*p***H**)
  pH_1 = *p***H** at the electrode tip (*p***H**)

$\text{pH}_{25\,^\circ\text{C}} = \text{pH}$ referenced back to $p\mathbf{H}$ at 25°C ($p\mathbf{H}$)

$\text{pH}_{span} = p\mathbf{H}$ span for calibrating the digital transmitter's output ($p\mathbf{H}$)

$\text{pH}_{0\%} = p\mathbf{H}$ at 0% of scale for calibrating the digital transmitter's output ($p\mathbf{H}$)

$\text{pH}_{100\%} = p\mathbf{H}$ at 100% of scale for calibrating the digital transmitter's output ($p\mathbf{H}$)

R_1 = measurement electrode glass resistance (ohms)

R_2 = measurement electrode internal fill resistance (ohms)

R_3 = measurement electrode cable insulation and connection resistance (ohms)

R_4 = reference electrode cable insulation and connection resistance (ohms)

R_5 = reference electrode internal fill resistance (ohms)

R_6 = reference electrode liquid junction resistance (ohms)

R_7 = resistance to ground at the measurement electrode tip (ohms)

R_8 = solution resistance between the measurement and reference electrode (ohms)

R_9 = resistance to ground at the reference electrode tip (Figure 1) (ohms)

R_{10} = solution ground resistance (Figure 1) (ohms)

R_{11} = shunt resistance that causes a loss in electrode efficiency (Figure 1) (ohms)

S_{eff} = electrode efficiency (%)

S_{slope} = electrode slope at 25°C (mv per $p\mathbf{H}$) (e.g., 59.1 mv per $p\mathbf{H}$)

T = temperature at the measurement electrode tip (°C)

T_{ref} = temperature reference point for the solution temperature compensation (°C)

Equation 1j shows that the effect of these potentials is additive. Whereas errors from changes in the parameters in Equations 1b and 1d result in horizontal shifts of the isopotential point, the extraneous potentials in Equation 1j result in a vertical shift of the isopotential point.. Usually, there is no attempt to distinguish and compensate for a shift in the isopotential point that is horizontal from changes in the condition of the gel layer versus a shift that is vertical from changes in the path resistance and condition of the reference electrode.

Application Effects (*Advanced pH Measurement and Control Fourth Edition*, ISA 2024)

Application effects, such as variable glass surface conditions, temperatures, ionic strengths, dissociation constants, streaming potentials, concentration gradients, and diffusion or liquid junction potentials, cause the $p\mathbf{H}$ measurement error in industrial process applications to be an order of magnitude larger than the normally stated accuracy, which is really for electrodes sitting in buffer solutions at laboratory conditions. Under the best of industrial conditions (e.g., dilute, low ionic strength solutions of weak acids and weak bases between 4 and 10 $p\mathbf{H}$ at constant temperature), the long-term accuracy, even with weekly calibration checks (average bias from a lab over a month of operation), is rarely better than +0.05 $p\mathbf{H}$.

Optimistic users and suppliers who provide one electrode per point in the process may believe they have achieved an accuracy of 0.02 $p\mathbf{H}$ or better. Results of installations with three electrodes per point in the process show that the error band from mixing noise and reference electrode drift over a month is, at best, 0.02 to 0.1 $p\mathbf{H}$ for a flat titration curve and 0.2 to 0.5 $p\mathbf{H}$ for a steep titration curve. Tests of 12 different electrodes of different and not the necessarily the best designs in a recirculation line of a laboratory tank showed that right after buffer calibration, readings differed by more than 0.5 $p\mathbf{H}$ for water and were reduced to about 0.25 $p\mathbf{H}$ when buffer solutions were added to the tank. The author's plant experience has been that after a buffer calibration, three

healthy electrodes will differ by 0.2 *p*H, where an electrode that is higher than the others may be lower within hours. This confirms some of the many advantages of middle signal selection (MSS) in terms of reducing the effect of these fluctuations and providing much more intelligence for calibration and diagnostics. If all three electrodes continually agree within 0.01 *p*H for more than a few hours in an industrial application, all three are coated, broken, or still have protective caps.

The maintenance practice of removing and buffering electrodes is costly and often counterproductive because it reduces measurement accuracy caused by damage to the glass electrode's fragile gel surface and the upset to the reference electrode's thermal and ionic equilibrium. It is possible to improve electrode performance and safety during *p*H maintenance, and reduce the cost of *p*H maintenance by an order of magnitude, through more realistic expectations and a better calibration policy that uses process standardization and relaxed goals.

The actual *p*H of the solution changes in response to the change in the ion dissociation constants with temperature. Until recently, compensation of only the change in millivolts generated per *p*H unit, or in other words, electrode temperature compensation, was offered. Microprocessor-based transmitters and receivers now offer solution temperature compensation. However, the relationship depends on the composition and operating conditions of the process stream. For strong base streams above 8 *p*H, the change is often about –0.3 *p*H per 10°C. Samples that cool down before they are measured in the lab will indicate a higher pH than the electrodes installed in the process. The potential of interest in *p*H measurement is the difference between the potential developed at the outer and inner glass surfaces of the measurement electrode as defined by Equation 1g. All other potential represents an error. Figure 1 shows the physical location of the potential ($E_1 - E_2$) and many extraneous potentials for a combination double-junction electrode, which has a reference electrode as a concentric ring around the glass measurement electrode. The combination electrode is popular because it reduces the installation and spare parts requirements. The internal salt bridge between the outer and inner junction of the double junction increases the time it takes for process ions to migrate to the inner chamber where the internal silver–silver chloride electrode is located. The measurement and reference electrode half-cell potentials in Equation 1j, which originate from an electrochemical reaction between the internal electrode and fill, are of opposite sign and ideally should be equal so their sum is zero. However, the half-cell potentials depend on the type of internal electrode, the internal fill concentration, and the electrode temperature. If the measurement and reference electrode type and fill are identical, the change in half-cell potential with temperature will cancel out unless a temperature gradient exists between the reference and measurement electrode locations. The measurement electrode normally has a silver–silver chloride internal electrode in a chloride buffer. The most common reference electrode also has a silver–silver chloride internal electrode and a potassium chloride electrolyte. The half-cell potential for a saturated silver chloride electrode varies with temperature from 193 mv at 40°C to 237 mv at 0°C. The measurement electrode glass bulb resistance is usually the largest resistance. It ranges from about 20 Mohms to 500 Mohms at 25°C, depending on the type and thickness of the glass. Rugged glasses, which are thicker than normal for greater resistance to breakage and abrasion and for a longer life in terms of time to failure of the silicon oxide matrix from penetration of the gel layer, often have a lower resistance per unit thickness so the increase in total resistance is moderated. The resistance dramatically increases at low temperature and can exceed 1000 Mohms for the type of glass used that is usually reserved for concentrated acidic solutions at high temperatures. Because a greater electrical resistance per unit thickness typically translates to a greater resistance

to etching and high temperatures, rugged electrodes generally are not suitable for hot alkaline solutions. However, advances are being made in glass formulations that increase the range of permissible operating conditions.

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The first-stage amplifier should have an input resistance 1000 times greater than the total resistance of the path from the measurement electrode through the reference electrode so the IR drop thought the amplifier is insignificant. The connection and insulation resistance of the measurement electrode cable should be at least 100 times greater than the path resistance to ensure that the parallel resistance to ground (R_3) at the measurement input to the field-effect transistor (FET) amplifier has a negligible effect.

Dehydration of the glass electrode can cause a significant increase in its resistance (R_1). However, the gradual penetration of the gel layer into the interior of the glass and thinning of the dry glass from the aging process or chemical attack should show up as a decrease in electrical resistance.

Measurement electrodes with a coated surface have a higher resistance (R_1), but the percentage increase is usually small and difficult to detect, particularly because the glass resistance is an exponential function of temperature per Equation 1q. Coatings are best detected as a dramatic increase in the time constant of the electrode because thin, almost imperceptible coatings greatly slow down the migration of hydronium ions. For example, a 1 mm coating on the glass can increase the T_{86} response time (time to 86% of the final response) of the glass electrode from 6 s to 5 min. Typically, the reference electrode junction resistance is only 1 to 10 kohms. The onset of a coating or partial plugging of the porous junction can easily cause the resistance (R_6) to more than double. However, salts from the process precipitating in the junction will be highly conductive and will not show up as an increase in resistance.

The resistances of internal electrode fills and external process fluids usually are only a few thousand ohms, so the potential drop from leakage current flow is negligible. However, high-purity water (i.e., distilled water, deionized water, or steam condensate) and nonaqueous solutions have an extremely high resistance (R_8) that approaches the resistance (R_1) of the glass.

A high total electrical resistance from applications with high-resistance glass at low temperatures (<20°C), with dehydrated glass, or in nonaqueous and pure water streams causes the *p*H

measurement to be sluggish and more susceptible to noise from ground paths, streaming potentials (static electricity), fluid velocity, and electrical interference.

The resistances in the path between the internal electrodes in the glass and measurement electrodes shown in Figure 1 are normally small compared to the glass measurement electrode resistance of 20 to 200 megohms. The current flow is extremely small, making the potential drop across these resistances negligible. The process fluid resistance (R_8) is negligible except for nonaqueous solvents or ultrapure water. The resistances to earth ground should be large enough to suppress noise from electromagnetic interference and ground loops.

A decrease in the high-impedance shunt resistance (R_{11}) can cause a loss of the electrode slope (efficiency). The degree to which the measured potential is decreased depends on the relative magnitudes of the glass electrode impedance and the shunt impedance. In one case of bad sensors with low shunt resistances, the sensors had low slopes (short-spanned) at room temperature but had adequate slopes for a higher temperature. This was due to the decrease in glass impedance at the higher temperature, which decreased the effect of the high-impedance shunt.

How bad can it be? If you look at the resistance (R_{11}) of the high-impedance shunt as a multiple of the resistance (R_1) of the high-impedance glass electrode ($R_{11} = n * R_1$), you can get an idea of how much the measured electrode efficiency would be lowered:

n	Efficiency
100	99%
50	98%
20	95%
10	91%
5	83% (bad electrode)

The glass electrode impedance significantly changes with temperature, whereas the shunt resistance does not. As the temperature increases, the glass electrode impedance decreases, what we might call the effective n value due to the shunt resistance increases, and the effect of the shunt decreases. Conversely, as the temperature decreases, the effect of the shunt increases.

The decrease in the shunt resistance (R_{11}) can be accelerated by aging from the exposure of O-rings and seals to a harsh process, which could attack the construction materials and introduce some leakage, as well as from the effects of prolonged heating on the internal potting materials, which could break down over time. The decrease has little to do with the glass electrode itself but rather is related to the integrity of the sensor construction over prolonged periods. It is also likely that at least some high-impedance shunting may be built into the sensor.

The liquid junction potential is typically the largest source of error in the 4 to 10 *pH* range if the measurement electrode is not extensively compromised as a result of dehydration, damage, age, or coating. If the measurement electrode is functional, the loss in efficiency does not translate to a large error in the neutral region.

Ions migrate from areas of high to low concentration by diffusion. As ions move into the porous junction of the reference electrode, they establish a voltage known as the *liquid junction potential* or *diffusion potential* (E_5). The more mobile ions accumulate in the junction, the faster they build up an excess charge that slows down the further accumulation of these ions. The potential E_5 and, consequently, the pH reading shifts until an equilibrium is reached. The potential E_5 for the standard KCl reference electrolyte is relatively small because the potassium (K^+) and chloride (Cl^-) ion electrolytes have about the same mobility, which means they accumulate in the junction at about the same rate. KCl electrolyte is not usually used in process fluids with compounds such as sulfides and nitrates that cause the formation of precipitates that clog the junction. A more common problem is the migration of process ions into the reference junction. Again, an excess charge of the more mobile ions accumulates until an equilibrium is reached that slows down the faster ions. The final potential $E5$ established from the migration of ions into the junction can be estimated by the Henderson equation that shows that the potential increases with the difference in the mobility of the positive and negative ions and the concentration of ions in the electrolyte and process solution. Thus, low and high ionic strength process solutions create a high junction potential.

Electrode Designs (*Advanced pH Measurement and Control Fourth Edition*, ISA 2024)

The movement of process ions into the reference electrode will also plug its junction and eventually contaminate its internal electrolyte. To reduce the rate of contamination at the internal silver–silver chloride electrode and the shift of potential E_4, smaller reference junctions, second internal junctions, gel electrolytes, porous solid internals, and flowing junctions are used. Smaller junctions increase the rate of fractional plugging of the junction and therefore reduce the time to a totally plugged junction. Double junctions, gel electrolytes, and porous solid internals increase the time required for the reference junction potential to reach equilibrium after being inserted into a process stream or for a dramatic change in the stream, which might occur during start-up or batch operation. Thus, these designs work a compromise between the conflicting needs for a fast, uncontaminated, and unplugged electrode. Note that extremely slow references will ignore short-term fluctuations in stream concentrations from imperfect mixing and may actually appear to provide a more stable (lower noise) reading. Also, if the electrode is immersed in the process by an automatically retractable assembly only for a relatively short time (1 or 2 min), the reference may not have had time to change its potential.

Solid references with small pore sizes help prevent the movement of small process particles into the junction. If this design is combined with an internal helical reference pathway, it is possible to have a large reference junction area to reduce the rate of fractional coating without a detrimental increase in the rate of contamination. However, the precipitation reaction of the silver or potassium electrolyte can rapidly occlude the small pores, so these electrodes should not be exposed to cyanides, bromides, iodides, sulfides, or nitrates. Methods to immobilize the electrolyte are used to reduce the migration rate of the electrolyte ions into the junction, thereby extending the reference's life and decreasing the rate at which the reference potential changes.

The fastest and most accurate reference electrode has a flowing junction. A constant small flow of electrolyte purges the junction and prevents the process from moving into the junction. The result is a small, quickly established liquid junction potential that can meet the demands of high accuracy and batch applications. However, the reference flow must be kept small enough so as to not

contaminate the process or excessively deplete the electrolyte by pressurizing the reservoir to maintain an appropriate pressure differential between it and the process. The external salt bridge provides the ultimate isolation of the reference's internal half-cell from the process. The additional installation and maintenance cost of this external pressurized reservoir makes it an unpopular choice with technicians unless it can be translated into reduced probe calibration and replacement or recognized process benefits from reduced variability.

A large surface area spherical glass bulb measurement and flowing junction reference electrode has the best accuracy because it has the fastest and lowest resistance glass and reference junction with the fewest extraneous potentials. A separate temperature probe also provides the fastest compensation for changes in process temperature. However, a flowing reference electrode requires pressurization and periodic filling of the reservoir. Furthermore, the accuracy and speed of response are only obtained with glass surfaces and reference junctions that are free from contamination, abrasion, and coatings.

Manufacturers generally offer several different glass formulations that are tailored to meet a process requirement. Glasses designed to be more rugged and handle chemical attacks from strong bases and strong acids tend to have higher resistance and consequential accuracy limitations, particularly for wide p**H** ranges. High measurement electrode resistance can also cause the p**H** measurement to be sluggish and more susceptible to noise from ground paths, streaming potentials (static electricity), fluid velocity, and electrical interference. Progress has been made in reducing the impedance of glasses so they can be used at lower temperatures.

Glass formulation is a highly proprietary technology with many undisclosed effects, compromises, and consequences as to the ability to handle process conditions. Corrosion strips away the outer gel layer while aging leaches out earth ions, increasing the glass impedance. Fewer earth ions make p**H** glass like regular glass. Both types of glass sense pH, but regular glass impedance is too high. More doping with earth ions to decrease impedance per unit thickness makes glass softer and more easily dissolved. Glasses used for thicker glasses in rugged glass electrode design use doping to reduce the total glass impedance with the consequence of being more susceptible to etching. Even with more doping, the extra thickness can make the glass impedance still too high at low temperatures.

A high-temperature glass formulation developed in the last decade can offer significant capability of measurement of higher temperature streams with much greater life expectancy, less drift, and incredibly faster response. The improvements are largely associated with greatly reduced glass aging. There can be more than a 100% increase in life expectancy for process temperatures of 50°C, 75°C, and 100°C and a three orders of magnitude decrease in the 86% response time of new versus general-purpose glass electrodes after exposure to high temperatures.

Originally, measurement electrodes used a spherical glass bulb design with a 0.2 to 0.5 mm thickness for the p**H** sensing membrane. Cracks tended to occur at the transition from the bulb to the straight side, although direct impingement of solids or debris caused cracks anywhere on the bulb. More durable semispherical and dome bulbs offer nearly the same performance.

The prevalent reference electrode in the 1970s had a liquid electrolyte and a flowing junction and was separate from the measurement electrode. In the 1980s, combination electrodes incorporating double reference junctions, as shown in Figure 1, created a throwaway concept by eliminating the need to refill reference solutions or troubleshoot separate electrodes. The electrolyte is a gel or is saturated in special wood or polymers to reduce the rate of contamination. The reference electrodes with porous solid materials impregnated with electrolyte are often called solid-state electrodes. In the 1990s, the pore size was reduced and the junction area increased.

In addition to the standard suite of measurement and reference electrodes just mentioned some special designs are intended to address application concerns that reduce the electrode's life or increase its installation and maintenance costs. Publications typically tout the advantages, and articles document the success stories. However, no electrode is perfect and a compromise is always at play. The following discussion will attempt to provide guidelines and explanations of the trade-offs based on limited testing, conversations with *p*H specialists, and application experiences in the 1980s..All the electrodes presented here were developed in that time frame, although improvements have certainly been made. Before an electrode is used in any difficult or demanding application, it should be installed in the process on a test basis and monitored closely.

A glass dome or hemisphere is used to provide a stronger shape and a thicker glass membrane. These "rugged glass" electrodes are designed to provide longer life by reducing the chance of cracking during installation and maintenance and from exposure to aggressive fluids where abrasion, etching, or corrosion is a concern. If the dome has a higher total electrical resistance, it may not be suitable for low temperatures and may exhibit a slower response. If the electrical resistance per unit thickness is reduced to lower the total resistance, the glass may actually be more susceptible to chemical attack.

Flat glass electrodes have been developed to minimize direct impingement that reduces abrasion and to maximize a sweeping action that reduces fouling. For viscous fluids, a fat glass electrode also eliminates the separation of the flow field and stagnation associated with the downstream side of a spherical bulb. These electrodes generally have a stated range of 2 to 12 *p*H. Streams with high sodium ion concentrations and ionic strengths introduce a greater error for flat glasses. The change in glass formulation to make it flat is detrimental to response and reliability, particularly at higher *p*H and temperatures. The thin flat surface is vulnerable to cracks. Flat glass electrodes have been reported to exhibit a significant undocumented and uncompensated temperature effect.

Pfaudler patented a measurement electrode made of Glasteel, a unique material formed by the fusion of glass and steel with an enamel coating. For operation below 5 *p*H, the probe has greater structural endurance, corrosion resistance, and a higher temperature rating of 140°C than conventional glass electrodes. It is designed to withstand the rigors of heat, pressure, and dynamic agitation in acidic reactors. This electrode must be paired with a transmitter that can be calibrated for a zero potential point between 1 and 3 *p*H. It provides a "relative" *p*H measurement in that the *p*H value sensed is not the same as that developed from a conventional *p*H electrode. However, its reproducibility and life expectancy may be better, and the lifecycle costs less because of its ability to handle higher temperatures and chemical attacks with reasonable accuracy in the 2 to 7 *p*H range despite a much higher initial cost for reactors. Nonetheless, the significant loss in performance at high *p*H and sodium ion concentrations is a concern.

Before the glass measurement electrode was developed for industrial measurement, the antimony electrode was used. Antimony is a hard, brittle material. Because of its toxicity, this electrode is no longer used. Other metal oxide electrodes have been used that also respond to *p*H by oxidation of their surface. Because oxidant accumulation on the electrode's surface deteriorates the measurement accuracy and repeatability, periodic cleaning is necessary. The electrode's response is nonlinear and requires narrow calibration spans or special polynomials for adequate accuracy. The metal oxide electrode is not recommended for operation below 2 *p*H. It is more temperature sensitive than the glass electrode. The approximate 50 millivolt output per *p*H unit increases from 1 to 3 millivolts per $^{\circ}$C as the *p*H increases. The isopotential point is about 2 *p*H, so transmitters with an adjustable isopotential point are required for temperature compensation. Finally, these are actually oxidation-reduction potential (ORP) electrodes. They respond to oxidizing and reducing species. The reading can be affected by less than one part per million (ppm) chlorine. Metal oxide electrodes are used as a last resort in applications where severe abrasion from slurries or etching from hydrofluoric acid or other process operating conditions cause a rapid glass measurement electrode failure [10]. A more accurate possibility, even in these cases, is using an automated retractable electrode to limit process exposure time. Also, an electrode whose tip does not protrude into the pipeline when inserted can minimize abrasion if the cross-sectional profile of acid and base concentrations does not introduce an error from the electrode tip not being in the pipeline.

Leeds & Northrup patented the DURAFET *p*H electrode. It uses an ion-sensitive field effect transistor ISFET instead of glass to provide a low-impedance, breakage-resistant measurement electrode. Most electrode manufacturers now offer an ISFET *p*H probe when glass is not permitted for applications less than 10 *p*H and temperatures less than 50°C. The characteristic drift of laboratory versions of ISFET *p*H sensors has been reduced. It is much faster than glass because the response is by an electrical field rather than moving hydrogen ions into a membrane. The sensor has integrated automatic temperature compensation and no sodium ion error or known ORP interference. It needs no hydration and uses a conventional reference electrode. The slope of about 59 mV per *p*H unit is close to that for glass, but the isopotential point shift necessitates a special calibration. The thin silicon nitride crystal covering is susceptible to degradation if faced into the flow. Unlike glass sensors, the ISFET requires no hydration and generally has a longer life if left dry. There has been some discussion but no documentation of the life expectancy in process solutions or the interference from stray electrical fields and ground potentials. Also, a partial process coating of the sensor due to fouling can cause a partial voltage response, unlike glass electrodes. Using an ISFET is not advisable for clean-in-place and in-line sterilization. A retractable ISFET is an option for these applications.

The construction features of a particular reference design in a reference electrode present a trade-off in the effort to quickly establish and minimize a constant junction potential while resisting contamination and coating. The user must decide which is most important for a given application. A decrease in the area of the reference junction reduces the rate of contamination but increases the fractional rate of coating and plugging. A thickening or solidification of the internal fill, the addition of double and triple junctions, and a decrease in the junction porosity slow down contamination but delay equilibrium and often increase the magnitude of the junction potential.

The most popular reference electrode has a silver–silver chloride inner electrode and a potassium chloride electrolyte. The potassium and chloride ions have about the same mobility, which

minimizes the junction potential from a difference in diffusion rates. However, the potassium chloride solution is saturated and tends to crystallize, especially at low temperatures, which reduces the diffusion rate and causes a drift in the associated potential at the junction. Also, silver from the silver–silver chloride internal element gets into the potassium chloride fill, reacts with sulfides and nitrates, and clogs the junction.

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Rosemount has also developed a reference electrode that has a replaceable outer reference electrode chamber that can be easily removed and refilled. The outer chamber electrolyte can be chosen to be more compatible with a process to minimize the liquid junction potential. Problems with coatings and contamination are readily dealt with by quickly replacing the outer electrode chamber. The electrode also uses the new high-temperature glass formulation.

In 1976, TBI patented a solid-state reference electrode that is nearly impervious to process contamination. The reference electrode consists of four wooden dowels saturated with potassium chloride solution. Process material must work its way up into the innermost wooden dowel, where the internal silver–silver chloride element resides, to create a drastic offset in the $p\mathbf{H}$ reading. Teflon is substituted for the dowel in contact with the process for applications requiring a sanitary surface or with chemicals that attack wood, such as hydrogen peroxide and hot, concentrated sodium hydroxide. Teflon is more difficult to keep saturated and slows down the time to equilibrium. This slowness is an advantage for continuous $p\mathbf{H}$ control, where it is desirable to ignore fluctuations in ionic strength from the steady state. However, it is difficult to get the electrode to match buffers within 0.1 of a $p\mathbf{H}$ for a two-point calibration. Because installation effects of more than 0.2 $p\mathbf{H}$ are normal, tight agreement with buffer solutions is not indicative of the electrode's installed performance. For high ionic strength process streams, high ionic buffers are recommended to precondition the electrode. A process calibration is essential for solid-state electrodes. For some batch applications, the reference does not have time to reach equilibrium, and $p\mathbf{H}$ errors of 0.5 $p\mathbf{H}$ and larger occur. In batch operations, it is important to use a wooden dowel, if possible, for the reference junction to make it faster.

Ingold patented a Xerolyte stiff polymer reference electrode. It uses an aperture diaphragm to provide direct contact between the process and the reference electrolyte. It has performance advantages in streams with high salt concentrations, emulsions, suspensions, proteins, sulfides, hot alkalies, and pressure fluctuations. However, it is not suitable for stream sterilization, large temperature changes, or extremely acidic media (below 2 $p\mathbf{H}$).

Great Lakes Instruments patented a differential reference electrode using a second glass measurement electrode (behind a double junction) in a buffer solution for the reference electrode. The glass bulb isolates the silver–silver chloride element of the reference from sulfides and nitrates

in the process. The buffer solution is chosen to be compatible with process fluids to ensure a constant buffer pH and a constant reference potential. A ground rod eliminates errors and noise from ground potentials. The smaller positive ions in the buffer solution tend to move through the reference junction out into organic and pure water streams. This creates an offset in the pH reading. The differential electrode has an excellent performance record in streams with inorganic acids and bases, and sulfides such as wastewater. The reference buffer solution has much smaller positive ions than negative ions, whereas most reference electrode fills are designed to have the same size ions. The positive ions can move out of the junction more quickly, causing a large pH offset from a large junction potential, particularly for organic and pure water streams.

Amagruss patented the Refex nonporous reference electrode that uses an ionic electrochemical conductive salt loaded into a polymeric matrix. There is no contact between the process liquid and the internal KCl electrolyte or Ag/AgCl half-cell. Because there is no porous junction, there is no migration of electrolyte ions or process ions into the junction. Consequently, there is no threat of contamination and no diffusion potential or time required to reach equilibrium. Thus, it is a candidate for batch, high and low ionic strength, and nonaqueous processes and streams with sulfides or cyanides that might cause precipitation. Also, coatings have no effect on accuracy other than via an increase in circuit resistance because there is no penetration or clogging of a junction. However, coating the glass bulb will dramatically slow down the response as it will for any measurement electrode. The reproducibility for different process conditions and replacement electrodes needs further documentation because a different attempt at this design concept suffered from a variability of matrix loading during manufacturing.

Installation (*Advanced pH Measurement and Control Fourth Edition*, ISA 2024)

It is difficult to predict the failure mode of pH electrodes because they can fail anywhere on or off the pH scale. However, the middle selection of three pH measurements will inherently ride out the first measurement failure of any type. It will also ride out a second measurement failure if it is in the opposite direction of the first. The implementation is straightforward in modern control systems because there is a Fieldbus function block that offers MSS that can be used in the field or in a field-based DCS. It is important to use the middle measurement and not a median or average measurement. In misguided attempts to do something better, configurations have been developed to reject one signal based on expert system–type rules and then average the remaining two measurements, but these rules cannot possibly cover all the bases and will eventually end up doing more harm than good. MSS is simple and foolproof. Equipment and piping should have connections for three probes. The user must realize that the multiple measurements will never agree and that this realization is the key to stopping chasing short-term transient deviations between electrodes. In the only case where multiple measurements were consistently observed to have the same readings, the electrode tips still had their protective caps filled with a buffer solution. If there are Coriolis mass flowmeters and the titration curve can be accurately identified or modeled, an online pH estimator can possibly be developed to replace one of the electrodes in a system with constant feed and reagent concentrations.

Using three electrodes and MSS also has numerous other advantages, as cited in the many Key Insights in this book. It will reduce noise and eliminate spikes much more effectively than a transmitter damping adjustment or a process variable filter without adding a lag time to the loop.

It will enable predictive maintenance based on the long-term trend of an electrode's deviation from the middle value. A single transmitter can be taken out of service without switching the controller to manual. A single electrode can also be manually or automatically retracted for cleaning, rejuvenation, and calibration with the controller in automatic unless there is a big spread between the remaining measurements. More intelligent maintenance reduces lifecycle cost, and better measurement performance offers benefits from better process efficiency and capacity.

Using two pH electrodes raises more questions than answers because they rarely agree, and there is no referee other than the lab, which has its own set of problems. However, installations of two electrodes are much more prevalent than three. Usually, a manual switch enables operations to select the current favorite, but the selection is based more on "war stories" than logic. High- and low-signal selectors are used when a downscale or upscale failure, respectively, clearly poses a greater safety hazard, but such predictions are not reliable and do not address the day-to-day deterioration in response time and accuracy. Some control system engineers attempt to develop more customized logic, but this is exceptionally difficult because of many challenges, and it is prone to do more harm than good. MSS and the collaboration of smart transmitters with automated maintenance, cleaning, control, and performance monitoring systems will lead to much better predictive maintenance and failure protection.

The dead time can be assumed to be equal to the residence time of the sample line because the time constant from the velocity profile is usually small compared to the total transportation delay so that the sample line is essentially plug-flow (no back mixing). Because the volume of the sample line is equal to the length multiplied by the cross-sectional area, the dead time can be decreased by decreasing the length or the diameter of the line or increasing the sample flow. The same relationship holds for the transportation delay from a pumped pipeline. A common mistake is to install a large agitator to reduce equipment dead time and then install the electrodes in a flow-through holder or chamber with a long length of intervening sample line or pumped pipeline so the resulting measurement dead time is greater than the equipment dead time. A heat exchanger in the sample line to lower the sample temperature or in the pipeline to remove the heat of neutralization can add significantly to the flow path volume and thus, the transportation delay.

It might seem that the submersion assembly is best for control. However, velocities below 1 fps dramatically slow down the electrode measurement response because of the increased boundary layer near the glass surface and promote the formation of deposits that can further slow down the measurement. The bulk velocity in even the most highly agitated vessels rarely exceeds 1 fps and is often much lower. The result is coating problems and a slow response. Removing a submersion assembly is cumbersome and time-consuming because of the assembly's long length. Jet nozzles help reduce the number of times the submersion assembly must be removed. Long assemblies in highly agitated vessels require a protective tube with side supports.

Before the 1990s, the most prevalent electrode installation assembly was a flow-through cell chamber or a simple pipe tee into which a probe was threaded. A small sample stream was diverted from the tank or pipeline, entered the bottom of the flow chamber, and exited the side. Strainers, filters, jet washers, and ultrasonic cleaners are added to reduce coating problems. Unfortunately, plugged strainers and filters can become as much of a maintenance headache as coating on the electrodes. Many options of how an electrode is installed in sample lines do not consider adverse

effects on measurement performance and dynamics . Winterizing all the fittings and items is difficult, and the temperature control is typically lacking to keep the sample temperature equal to the process temperature. Today sample systems are viewed as undesirable because of the additional transportation delay and increased installation and maintenance costs.

The development of the retractable injector probe, enabled inserting electrodes into and removing electrodes from pressurized vessels and pipelines. The high velocity in pumped pipelines decreases the coating rate and the time constant of the electrodes. The electrodes can be removed, even though the pipeline is pressurized, by slightly loosening the fitting that grips the electrode's metal sheath, slowly withdrawing the sheath until it clears the ball valve, closing the ball valve, and withdrawing the sheath the remaining distance. In some respects, this type of assembly is safer than a flow chamber with an integral terminal enclosure because the sealing method is easily checked and any leaks are visible. The restraining strap must never be removed to prevent the probe from becoming a projectile because of worn or missing fittings. A tee and an additional ball valve can be provided to flush the assembly before removing the sheath. The retractable assembly enables installing electrodes in pipelines for vessel recirculation and downstream of static mixers, and it eliminates the need for isolation and bypass valves.

The best location, except for very abrasive service, is a recirculation line close to the outlet. Installing an electrode downstream of the pump is preferred because the strainer will block and the pump will break up clumps of material that might break the electrodes. The retractable probe provides the most straightforward and economical solution. The electrode tips must be pointed down to prevent the air bubble inside the electrode fill from residing in the tip and drying out the inside surface. An installation angle of 20 to 90 degrees from horizontal is sufficient to keep the bubble out of the tip. Some electrode designs eliminate the bubble via a flexible diaphragm for fill contraction and expansion.

Retractable injector–type probes are usually installed in a horizontal pipeline unless vertical lines are needed to help drain solids. Parallel lines enable the probes to be isolated, but the velocity and distribution of solids are not equal. Consequently, there tends to be an offset and a difference in life expectancy and coating rate between probes. Installing probes in series ensures that each probe sees the same mixture and velocity, which leads to more consistent readings and maintenance requirements. For coating and abrasive service, the slot or hole in the shroud is facing into and away from the flow stream, respectively. For all lines, the velocity is adjusted, and in vertical lines, the angle of insertion is varied based on whether the goal is to prevent coatings or abrasion.

Electrodes do best if they are left in service, exposed to and in equilibrium with the process. In severe services where the rate of fouling or degradation is excessive, the electrodes must be removed and serviced periodically. Automated procedures provide much more consistent results, especially when it comes to $p\mathbf{H}$ electrodes. Automated retractable assemblies have double-acting pneumatic piston actuators that can withdraw and insert an electrode on command by energizing or de-energizing solenoid valves on the supply and exhaust air lines. In the retracted position, the electrode tip sits in a chamber. Solenoid valves on various solutions to the inlet of the chamber are energized to flush, clean, calibrate, and soak the electrode. A solenoid valve on the outlet drains the chamber.

The following is a compilation of common installation pitfalls.

- The measurement electrode cable is frayed or its connector is wet. (A low impedance path to ground is created.)

- The shield to the preamp is grounded. (A ground loop to the solution ground is created.)

- There is no provision for continuous circulation and self-draining the pipeline or sample line. (Electrodes sit in stagnant process fluid.)

- The temperature measurement of the process fluid at the electrodes is not transmitted. (The solution temperature compensation in the control room and in the lab is inaccurate.)

- The sample line is not winterized. (The sample line freezes during water batching or when the sample flow is shut off.)

- There is no throttle valve and no meter for adjusting or measuring velocity at the electrodes. (Partially plugged lines or improper velocities are not detected.)

- The electrode tips are in the top of a line or near the surface of a vessel. (Air bubbles collect near the electrode tips, drying out the internal gel layer and causing a noisy signal.)

- The slot in the sheath of an injector probe is pointed into the flow for a slurry stream. (Electrode abrasion develops.)

- The slot in the sheath of an injector probe is not pointed into the flow for a fouling stream. (Electrode coating develops.)

- The electrodes are not kept wetted for batch or intermittent operations. (Dehydration of the electrode occurs.)

- The submersion electrode assembly is near the bottom of the vessel and is not supported. (The assembly breaks due to the whipping action from agitation.)

- The submersion electrode assembly is installed in a stilling well. (The response is sluggish, and a coating develops due to insufficient velocity past the electrodes.)