# The Glass pH Electrode

by Petr Vanýsek

Editor's note: We are pleased to introduce a new magazine column that aims to take the reader back to the classroom. This series of tutorials will be written by experts for a non-specialist audience. Please let us know what you think of this new feature.

A glass electrode is perhaps the most successful and ubiquitous electrochemical sensor. It provides information about the activity of hydronium ions, H_3O^+, in water. Because water, which mildly dissociates to H_3O^+ and OH^- ions, is the most common solvent medium, and chemical reactions in water largely depend on H_3O^+ activity, the ability to measure it is essential. And conversely, because H_3O^+ activity, or rather, its negative logarithm, the pH, is so easy to measure, pH is the most commonly monitored and recorded parameter of liquid samples.

A glass electrode (Fig. 1) is actually a device, not an electrode in an electrochemical sense of the word. It consists of a glass bulb membrane, which gives it its name and an electrically insulating tubular body, which separates an internal solution and a silver/silver chloride electrode from the studied solution. The Ag/AgCl electrode is connected to a lead cable terminated with some connector that can hook up to a special voltmeter, the pH meter. The pH meter measures the potential difference and its changes across the glass membrane. The potential difference must be obtained between two points; one is the electrode contacting the internal solution. A second point is obtained by connecting to a reference electrode, immersed in the studied solution. Often, this reference electrode is built in the glass electrode (a combination electrode), in a concentric double barrel body of the device. Figure 2a shows a diagram of such a device. Figure 2a, the combination electrode and Fig. 2b, a glass electrode and separate reference electrode, are functionally identical. It is a common misconception that the combination electrode (Fig. 2a) requires only one lead, fostered because the round coaxial lead to the electrode looks like a single wire. This is not so. In any potentiometric measurement, and pH measurement is an example of one, two inputs, one of which is a reference point, are required. The completed glass electrode with a reference electrode cell is represented by the electrochemical shorthand

Ag/AgCl | HCl | glass || probed solution | reference electrode (1)
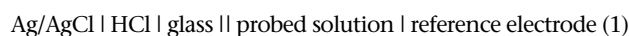
The potential difference relevant to pH measurement builds up across the outside glass/solution interface marked ||. The key functional part, the glass membrane, is manufactured by blowing molten glass into a thin-walled bulb with a wall about 0.1 mm thick. The bulb is then sealed to a

FIG. 1. Schematics of a glass electrode.

thicker glass or plastic tube, and filled, for example, with a solution of HCl (0.1 mol/dm^3). In this solution is immersed a silver/silver chloride electrode with a lead to the outside through a permanent hermetic seal. The filling solution has constant Cl$^-$ concentration, which keeps the Ag/AgCl inner electrode at fixed potential.

The pH sensing ability of the glass electrode stems from the ion exchange property of its glass membrane. Glass is mostly amorphous silicon dioxide, with embedded oxides of alkali metals. When the surface of glass is exposed to water, some Si–O- groups become protonated

$$Si\text{-}O\text{-} + H_3O^+ \equiv Si\text{-}O\text{-}H^+ + H_2O \qquad (2)$$
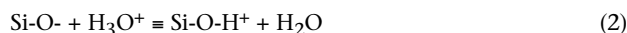
The exchange of hydronium (or written as proton, H^+) between the solid membrane and the surrounding solution, and the equilibrium nature of this exchange, is the key principle of H_3O^+ sensing. As with any interface separating two phases between which ionic exchange equilibrium is established, the glass membrane/solution interface becomes the site of a potential difference

$$E_{\text{glass wall/solution}} \sim |RT/2.303F \log a(H_3O^+)| \qquad (3)$$

where R is the molar gas constant 8.314 J mol^{-1} K^{-1}, T is the temperature in kelvins, F is the Faraday constant 96,485.3 C, 2.303 is a conversion between natural and common logarithm, and $a(H_3O^+)$ is the activity of hydronium, which can be at lower concentrations equated with its concentration. At 30°C the value of $RT/2.303F$ is approximately 0.060 V.

The glass membrane has two wall/solution interfaces and there is potential buildup on each of them, with opposite polarity. But the pH inside the bulb is constant, because the internal solution is sealed. Therefore, the inner surface potential is constant, adding merely to an offset to the overall potential of the device. Additional contribution to the offset comes from potentials of the inner solution electrode, and the reference electrode, which are also constant. The changes in the device potential are therefore due entirely to the pH changes of the outside solution and the potential of the glass electrode/reference electrode setup is

$$E_{\text{glass electrode}} = E' + RT/2.303F \log a(H_3O^+) \qquad (4)$$

Where E' represents the sum of the constant offset potentials of the inner glass surface/solution and the two Ag/AgCl electrodes. At 30°C the potential of the glass membrane changes by about 60 mV for each one unit of pH (*i.e.*, a tenfold activity change).

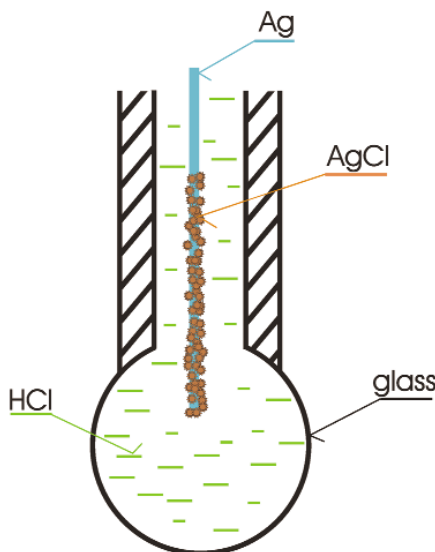The possible range of hydronium activity encountered in aqueous solutions is large, as much as 10 to 10^{-15} mol/dm^3.

To encompass such a wide dynamic range, a logarithmic scale was established, defining the pH of a solution as

$$pH = - \log a(H_3O^+) \qquad (5)$$

The negative sign assures that pH of most solutions, except extremely acidic ones, is always positive. It is fortuitous that the potential of the glass electrode (Eq. 4) is also a logarithmic function of hydronium activity; therefore, the potential of the glass electrode is a linear function of pH

$$E_{\text{glass electrode}} = E' - RT/2.303F \; pH \qquad (6)$$

The $E_{\text{glass electrode}}$ is measured with a pH meter, a voltmeter with circuitry allowing direct readout of pH. The meter subtracts the potential offset E'. Although it could be calculated, it is more practical to calibrate the glass electrode using buffers. For example, if two buffers are used in sequence, one at pH 7 and another at pH 4, it is also possible to calibrate the actual slope of Eq. 6. Although it is mathematically given as $(RT/2.303F)$, the behavior in the presence of interfering ions or with deteriorating glass electrode is not always that ideal. The correction for temperature (T) is also made in a two-buffer calculation. Increasingly, glass electrodes and hand held pH detectors, have built-in temperature probes, linked to an automated electronic temperature correction. Because the pH of standard buffers is available to two decimal places, measured pH should be reported to no more than two decimal places, despite that most pH meters can display three places or more. Practical reproducibility is about ± 0.05 units.

The circuit across which the pH meter measures the potential difference has high electric resistance. Even though the resistance is minimized by blowing the glass very thin and doping it with a mix of alkali metals, the circuit resistance is still 10^7-10^9 Ω, which is too high for a normal voltmeter; a special kind with high input impedance is needed. The ubiquity of glass electrode pH sensors was made possible through advances in electronics. The first significant step was introduction of a high input impedance vacuum tube amplifier in 1928; however, a key to miniaturization and low cost came through introduction of field-effect transistors and subsequently the knowledge to integrate them with the digital signal processing circuitry on a single chip. Modern pH meters, combining the glass membrane sensing element, electronics, and a display, are now the size of a pen, no larger than a glass electrode of only a few years ago.

Still, the glass electrodes of today share with the glass electrodes of yesterday both their working principle and their limitations. A common interference with sensing hydronium comes from ions of similar size, notably the alkali metals. The interference is somewhat alleviated by using specialty lithium glass, with sites too small to fit Na^+ or K^+. Alkali metal interference is not the only complication. In solutions of concentrated alkali hydroxides not only the metal ion concentration is high, the activity of H_3O^+ is small, making equilibration more complicated. And on top of that, strong alkaline solutions etch and possibly permanently damage glass surfaces. Fluoride is another ion that can physically damage glass. Additionally, solutions with proteins, that adsorb on surface, or solutions of ions of more noble metals (Ag, Cu) that could reduce and deposit on the glass surface, should also be avoided.

FIG. 2. Measurement with (left) a glass electrode, combination style; and (right) a separate glass electrode and a reference electrode.

The lore of proper glass electrode handling is rich and often irrelevant. The glass of the membrane has evolved, the pH meters are more reliable, and the electrodes have become more affordable. The glass membrane of the past must have remained wet for proper hydration. That is not true for the modern type and it is recommended that, if not used for several days, the electrodes are allowed to dry. They should be rinsed thoroughly, though, because a drying crust of solids would crack and destroy the membrane. Prior to initial use a glass electrode must be soaked in water to regenerate the hydrated layer. But the elaborate procedure for early electrodes has changed to a short wait for the modern counterparts. There are also recipes describing how to bring an ill-performing electrode back to life. Described are such heroic procedures as a quick dip in hydrofluoric acid. It is hardly worth the effort though, because some modern devices come with a replaceable, if not disposable, glass membrane tip. The replacement cost is often less than would be the wage paid to someone trying to rejuvenate a flawed electrode. However, these practical recipes remain great lessons in chemistry and materials science.

The glass electrode has been around almost a century. In 1906 Max Cremer[1] during his studies of liquid interfaces blew in a flame a thin bubble at the end of a glass tube and measured the potential difference between one liquid inside and a different one on the outside. Fritz Haber (Nobel Prize winner for the synthesis of ammonia) and Zygmunt Klemensiewicz[2] measured in a series of experiments the potential difference on two sides of a glass membrane; they discovered that the potential is a function of proton activity and coined the name glass electrode.

References

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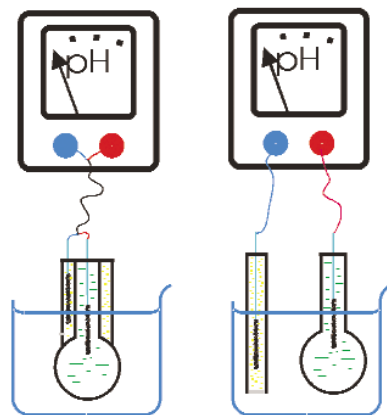2.   F. Haber and Z. Klemensiewicz, *Z. Physik. Chem.,* **67**, 385(1909).

About the Author

PETR VANÝSEK *was born and educated in Czechoslovakia, where he received his PhD in physical chemistry while working on electrochemistry of liquid/liquid interfaces. His academic experience includes postdoctoral work at the University of North Carolina, a year as a faculty-in-residence at the University of New Hampshire, and two sabbaticals; at The University of Calgary and at Aclara BioSciences, where he spent an additional year on a leave of absence. He has been a regular faculty member at the Department of Chemistry and Biochemistry at Northern Illinois University since 1985.*

Dr. Vanýsek's research interests are in physical and electro-analytical aspects of interfaces between immiscible solutions (which coincidentally dates back to the invention of the glass electrode), studies of corrosion and development of sensors, microfluidics, and fuel cells. He is focused on detailed understanding of interpretation of impedance. Through his teaching assignments he has became an expert in many aspects of analytical measurements, including those of proper use of pH instrumentation.

Dr. Vanýsek has been a member of The Electrochemical Society since 1986 and presently serves as its secretary.