Product Introduction

Industrial Gel-Filled pH Electrode 6155

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We have developed "Industrial Gel-filled pH Electrode 6155". One of the features of this product is that polymer gel including potassium chloride (KCl) solution, instead of KCl solution itself, is filled inside of its reference electrode. This improves usability during maintenance because there is no need to replenish the internal solution. Besides, water pressure resistance is also improved comparing with general liquid-filled electrodes. Another feature is double structure of liquid junction, which reduced measurement errors in fast-flowing low conductive samples to less than one tenth of our existing electrodes. We are proud to provide satisfying pH measurement to further a wider range of customers by the development of this product. In this article, we explain the feature of the 6155 electrode in detail, and introduce examples of measurements in some fields.

Introduction

HORIBA group has been developing and providing pH electrodes over 60 years since Masao Horiba, who is the founder of HORIBA, developed a first glass pH electrode in Japan. Now, HORIBA pH electrodes are used for water quality management in various fields, such as water and wastewater treatment plants and process water treatment facilities in many kinds of factories. In such fields, pH electrodes are frequently placed in harsh environment, and are required accurate measurement with continuity and durability. In order to meet the needs of diverse fields, we have been lining up many kinds of pH electrodes, such as hydrofluoric acid-resistant electrodes and alkali-resistant pH electrodes.[1]

Whereas, customer demands are so diverse that we have still challenges for improvement in order to use pH electrodes more easily in a variety of site. For example, simplification of maintenance is sought by many customers because general pH electrodes require laborious operations during maintenance like calibration and washing. Also, the pH electrodes generally have problems such as short life at a site with high pressure, and measurement error at a site with high flow rate. Therefore, we have developed "Industrial Gel-filled pH Electrode 6155" that has advantages in the following three points (Figure 1).

- Usability (Ease of maintenance)
- Pressure resistance
- Accuracy of low conductivity sample measurements

In this article, we explain the advantages of the 6155 electrode comparing with general electrodes, and introduce examples of measurement in some fields.

Figure 1 A photographic image of the industrial gel-filled pH electrode 6155.

Structure of pH electrode and the measurement principle

A general method of glass electrode is adopted for pH measurement of 6155 electrode. At first, the method is explained as follows.[2]

A glass pH electrode is composed of a glass electrode and a reference electrode (Figure 2). Hydration layers are formed in the wetted part inside and outside of response

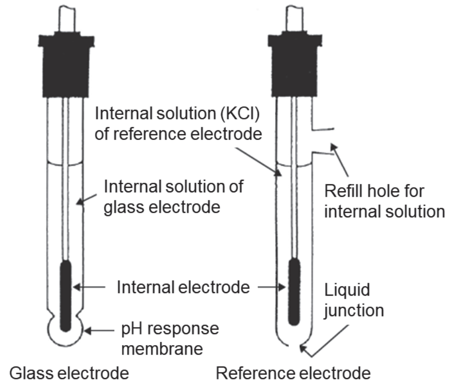

Figure 2 A structural image of a fundamental pH electrode.

glass membrane when a glass electrode is soaked in a sample solution. As a result, an electric potential is generated proportional to the pH difference between internal and sample solution. A reference electrode, internal potassium chloride (KCl) solution is connected with a sample solution via liquid junction, generates constant potential regardless of pH. The pH is calculated by Equation 1, depending on potential difference between the glass electrode and the reference electrode, and liquid temperature.

$$\mathrm{pH(X)} = (Ex - Es)/(2.3026\mathrm{RT/F}) + \mathrm{pH(S)} \quad \cdots\cdots\cdots \quad (1)$$

pH(X): pH of a sample solution
pH(S) : pH of a standard solution for calibration
Ex: Potential difference measured in a sample solution
Es: Potential difference measured in a standard solution for calibration
R: Gas constant
T: Absolute temperature
F : Faraday constant

Most of current pH electrodes are composite pH electrodes composed of a glass electrode, a reference electrode, and a temperature sensor (Figure 3). The 6155 electrode is also the composite pH electrode.

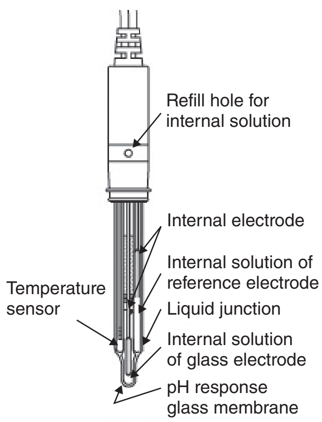

Figure 3 A structural image of a composite pH electrode.

Features and advantages of the 6155 electrode compared with general electrodes

In this section, we explain structural features of the 6155 electrode and its advantages comparing with existing pH electrode of our company.

Good usability

One of the features of the 6155 electrode is that polymer gel including saturated potassium chloride (KCl) solution is filled inside of its reference electrode instead of KCl solution (Figure 4). Since this polymer gel has a strong binding property and is insoluble in water, it has the following advantages.

(1) Chemical resistance.
(2) No containing of microbial nutrition (Mold free).
(3) No flowing out into sample solution (Long life).

Also, the KCl saturation state is maintained for long term since KCl granules is also added in the polymer gel. Accordingly, the 6155 electrode can be used in various kinds of fields for long term without refill of internal solution.

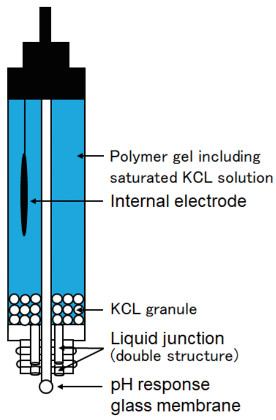

Figure 4 A structural image of the 6155 electrode.

Gel-filled pH electrodes have advantages of usability in regard to installation, and maintenance like calibration and washing. Generally, a refill tank for internal solution is installed to conventional liquid-filled electrodes since securing of internal solution volume is necessary in order to extend maintenance cycle (Figure 5). The holder of the electrode with KCl tank becomes heavy, but if the holder is not kept vertical, the internal solution spills out of the refill tank. Therefore, it is not easy to perform the maintenance by one person, and it may be dangerous at a site where a working space is not sufficient (Figure 6 left). On the other hand, the gel-filled 6155 electrode does not need to be attached the refill tank. As the result, the electrode and its holder become lightweight. Accordingly,

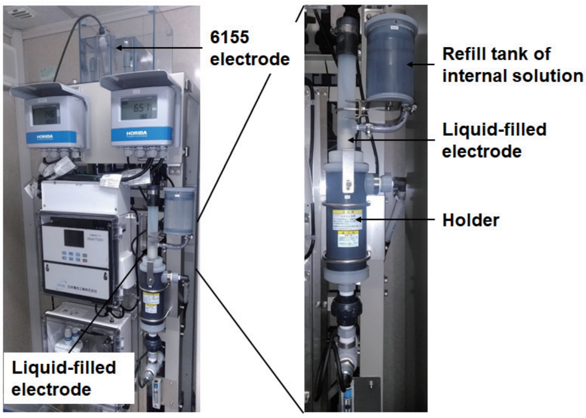

Figure 5 Photographic images of an general installed liquid-filled electrode of our company and a 6155 electrode.

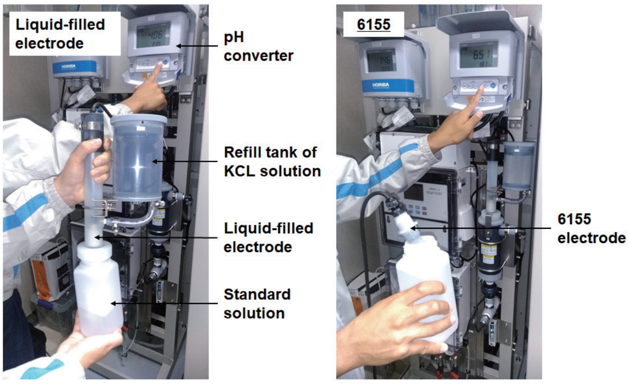

Figure 6 Photographic images of calibration of a general liquid-filled electrode of our company and a 6155 electrode.

the work at the time of installation is simplified by reduction of number of parts as well as ease maintenance by one person is possible (Figure 6 right).

Improvement of pressure resistance

As described above, inside of a reference electrode is connected with sample solution via liquid junction. In liquid-filled electrodes, sample solution backflows into the inside of the electrode when pressure is applied from the sample side. This provokes dilution and/or disruption of the internal solution, resulting in inaccurate pH measurement. We deal with the problem by pressurizing the internal solution toward the sample side, however, it is difficult to control the pressure completely. The backflow was not prevented when the sample pressure exceeds the pressurized value set by the user. Whereas, outflow of the internal solution is accelerated when the sample pressure is lower than the pressurized value. In this case, shortening the maintenance cycle becomes a problem.

With regard to the 6155 electrode, the water insoluble polymer gel, which hardly resolves to the sample side, is filled inside of the reference electrode without any gaps. Therefore, the backflow of the sample solution hardly occur. Accordingly, accurate pH measurement can be performed for a long period with few maintenance even under high-pressure condition such as in a closed pipe line. In fact, it has been confirmed that the 6155 electrode is used until 0.7 MPa of pressure, which is about seven times as much as atmospheric pressure.

Accuracy of low conductivity sample measurements

General pH electrodes occur measurement error when measuring fast-flowing sample solution. It is assumed that the measure cause is flow potential generated when liquid moves inside the capillary (Figure 7 left). Degree of the measurement error caused by the flow potential is notable when conductivity of the liquid in the capillary is low. Therefore, we should consider the error, in case solution containing little ions such as ion-exchange water, groundwater, and tap water is measured.

We adopted inside the capillary (Figure 7 left) a double structure liquid junction composed of a porous ceramic part, generally used as liquid junction, and a porous polyethylene (PE) part for the 6155 electrode. The flow potential could be reduced even in the low electric conductivity sample since the flow rate is reduced inside of the PE part (center in Figure 7). We investigated pH difference with and without flow rate, using sample solution with 100 μS/cm of conductivity, which is as low as tap water. It is revealed that the pH difference of the 6155 electrode was less than 1/10 of other three kinds of conventional electrodes (Figure 7 right). Besides, the 6155 electrode can measure flowing samples with 10 μS/cm of conductivity within 0.1pH difference under normal pressure condition,

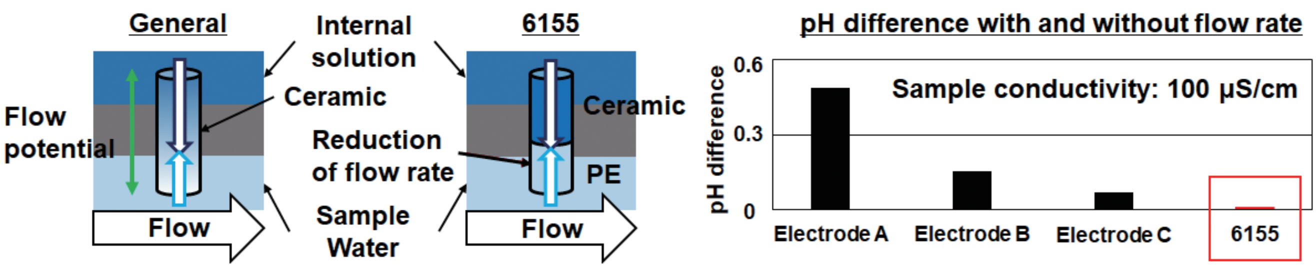

Figure 7 Illustration images of liquid junction part, and pH difference with and without flow rate, in regard to general electrodes and a 6155 electrode.

as long as keeping liquid junction to clean.

Measurement examples in some fields

Field evaluation revealed that the 6155 electrode can continue stable pH measurement in many kinds of samples. Further, even in the field where various kinds of dirt such as inorganic, organic, and microorganisms pose a problem, it can be used with a low maintenance frequency by combination with our automatic cleaners, such as an ultrasonic cleaner and a water jet cleaner. Examples of the sites where the field evaluation were performed are shown below.

- Intake of water purification plant with a sample electric conductivity of about 100 µS/cm
- Reverse osmosis membrane treatment process with a sample pressure of 0.3 MPa
- Groundwater with a sample pressure of 0.5 MPa and an electrical conductivity of about 40 µS/cm
- Aeration tank in a wastewater treatment facility (Figure 8)
- Anaerobic treatment process of wastewater treatment facility (combined with ultrasonic cleaner)
- Factory drainage (combined with water jet cleaner)

Figure 8 shows a comparison between the reference electrode standard potential of the 6155 electrode and a gel-filled pH electrode made by other company, electrode X, in the aeration tank of the wastewater treatment facility. The standard potential depends on the KCl concentration of the internal solution (or gel), and is generally around 0 mV under the regular condition. The standard potential of the 6155 electrode (pink line) shows 0 ± 10 mV for 3 years, which means that the pH shift caused by the reference electrode is within ± 0.15pH. Also, there are not confirmed drift tendency of the potential for 3 years. Electrode X also showed the almost same pattern as the 6155 electrode for first one year, however, there are confirmed a potential drift to the positive direction after that. One and a half years later, the standard potential shifted to more than 30 mV (0.5 pH). This is attributed to dilution of KCl concentration in the polymer gel due to sample invasion from liquid junction.

Since the polymer gel of the 6155 electrode is a water-insoluble gel having excellent chemical resistance, change in composition and reduction of the included KCl concentration by sample invasion hardly occur. Further, the KCl-saturated state in the polymer gel is maintained even if the sample is mixed, since KCl granule is contained there. The granules gradually dissolve by contact with the sample solution, but the amount are designed to withstand the continuous immersion for more than two years at normal temperature and pressure. By this field test, it is confirmed that the 6155 electrode actually had a lifetime of more than 2 years although it may depends on environment and kinds of sample.

In addition, a combination of the 6155 electrode and our automatic ultrasonic cleaner was evaluated in an anaerobic treatment process of wastewater treatment facility. According to the customer, existing pH electrode made by other company had to be manually cleaned every day for accurate measurement since dirt is remarkably adhered to the response membrane and liquid junction. The continuous measurement values of the 6155 electrode and the existing electrode were compared at the same site. The measurement value of the 6155 electrode reacted dynamically at timings when no shift was observed in the existing electrode. According to the customer, this indicates that the 6155 electrode was accurately following pH shift of the sample. Further, it was found that the 6155 electrode can continue accurate measurement for more than two weeks at this site without cleaning. In the result, the cycle of manual cleaning by the customer could be significantly reduced. Now, the 6155 electrode have been implemented for more than six months at that site. The customer has commented as "Excellent measurement have been continued."

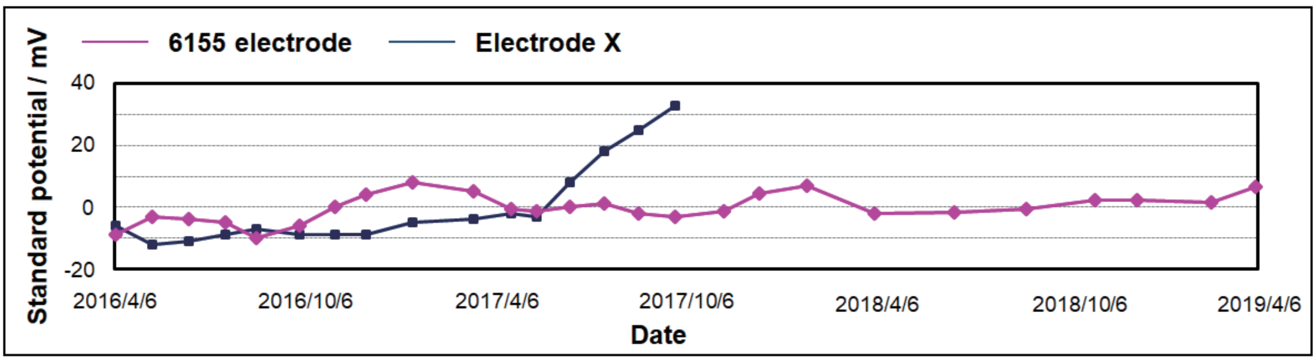

Figure 8 Comparison of continuous measurement of reference electrode standard potentials in activated sludge layer of wastewater treatment facility between the 6155 electrode and pH electrode made by other company.

Conclusion

pH electrodes have been used for various purposes for long time since they were firstly produced by Beckmann in 1935 in the world, by Masao Horiba in 1950 in Japan. However, there are a lot of rooms for improvement in order to meet diverse requirement in various fields. We have developed “Industrial Gel-filled pH Electrode 6155” which has advantages of usability, pressure-resistance, and low-conductivity sample measurement. We proud of providing pH measurement satisfied for further more customers, although we have ever been lining up various kinds of pH electrodes. We will make further efforts to contribute water quality by providing many sensors that matches customer’s requirement.

* Editorial note: This content is based on HORIBA’s investigation at the year of issue unless otherwise stated.

References

[1] Susumu Yamauchi, “Introduction of the New H-1 Series Water Quality Instruments”, *Readout*, **37**, 88 (2010)

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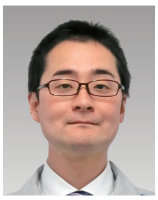

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