

Inverse Model of the Glass pH Sensor

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Introduction

The concentration of ion H^+ (pH) in solution plays very important role in chemical, biological and physical processes. Since Cremer (1906) first reported the pH response of oxide glasses, many theoretical researches about the glass electrode and its applications have been carried out. The glass electrode is stable mechanically and chemically and can be used in the wide range of solvents. In spite of new developments of semiconductor sensors and optical sensors for pH measurements (Bakker, 1998), the glass electrode is still of great practical importance.

The glass electrode is relatively fast and can be applied effectively in on-line measurements. However, for some applications such as identification tanks (Sung et al., 1995; Obut and Ozgen, 2008), end-point estimations and auto-titrators, faster responses will be preferable. The detailed mechanism of glass electrode is still questionable. Roughly, the dynamic response of glass electrode consists of quick response to a quasi-equilibrium and slow drift due to ion permeation through the glass membrane (Kohler et al., 2005). The former, response to the quasi-equilibrium, can be explained through the equivalent circuit having a very high internal resistance and a capacitance (Buck, 1968). Time constant of the glass electrode is the time that the capacitance is charged through the very large internal resistance. Here a measuring method that reduces this time by an order of magnitude is proposed. External voltage is introduced to charge the capacitance. It is compared and controlled to trace the glass pH electrode voltage by the integral controller.

Glass pH Sensor

A typical pH combination electrode consists of glass and reference electrodes in one body. It has a thin glass bulb which is sensitive on the pH of solution. This pH-sensitive glass membrane has a typical resistance of $10^8\Omega$ and capacitance of 10^2pF . Fig. 1 shows a rough equivalent circuit of the glass pH electrode. Because capacitances are due to electrodes and electrical double layer of solutions and are distributed throughout elements of the pH sensor body, the equivalent circuit of Fig. 1 is approximate and will be effective for low frequency operations.

The voltage of the ideal pH electrode changes by 59.16 mV per each pH unit change at 25°C (Harris, 2007). It can be measured through operational amplifiers with input resistance over $10^{12}\Omega$ and very low bias current. For a step change of pH, the voltage output of glass pH sensor shows responses as shown in Fig. 2. This dynamical response is due to times to charge the capacitance through the resistance of the glass membrane. Times to reach the steady state pH values can be as large as 5 sec for some pH sensors and they can be too large for some applications. A method to reduce these times is investigated.

Responses for the External Voltage Forcing

Here an external voltage forcing as shown in Fig. 3 is considered. Dynamic model for this system can be expressed as follows:

$$E_b(s) = \frac{R/(R+R_1)}{\tau s + 1} E_a(s) + \frac{R_1/(R+R_1)}{\tau s + 1} E(s) \quad (1)$$
$$\tau = R_1 C \left(1 + \frac{R_1}{R} \right)$$

When E_b is not connected (R_1 is infinite), the time constant τ in Eq. (1) becomes RC . That is, the time constant for the step change of E (the voltage of glass pH sensor) is RC (multiplication of the internal resistance and the capacitance). Responses will be like Fig. 2.

When R_1 is much smaller than R , the time constant τ in Eq. (1) becomes $R_1 C$. Smaller time constant will make responses for voltage changes of E and E_a be faster. Fig. 4 shows this. However, the pH sensor output E_b at the steady state is $R/(R+R_1)E_a + R_1/(R+R_1)E$, which is dependent of R . Because R is

not known in advance and time varying, especially for the change of temperature (Buck and Krull, 1968), a simple measurement of the voltage E_b at the steady state for a constant E_a cannot be used to estimate E . To solve this problem, methods to find the internal resistance R and the sensor voltage E simultaneously with two or more experiments for different forcing voltages of E_a are invented (Koluvek, 1995). A square wave with sufficient period to ensure steady states of E_b can be used for measuring E and R continuously.

Proposed Measurement Circuit

Methods with external alternating-current voltages make electric currents flow through the glass pH electrodes. It is much different from the conventional zero current measurement. Here, a method which is similar to the conventional zero current measurement of pH is proposed. A circuit for this is shown in Fig. 5. Q_1 is an instrumental amplifier with very low input bias current and very high input resistance. Its gain is adjusted by the resistance R_2 and measures the current flowing to the glass pH electrode. The circuit around Q_2 is an integrator. This feedback system is an integral control system which will make the current to the glass electrode be zero. It will make E_a (Output) trace E continuously. Changing feedback loop gain, time constant for the step change of the glass pH electrode E can be made small.

Conclusion

A simple method to make time constant of the glass pH electrode be small is proposed. It can trace the voltage of glass pH electrode and measure it at the condition of near zero current.

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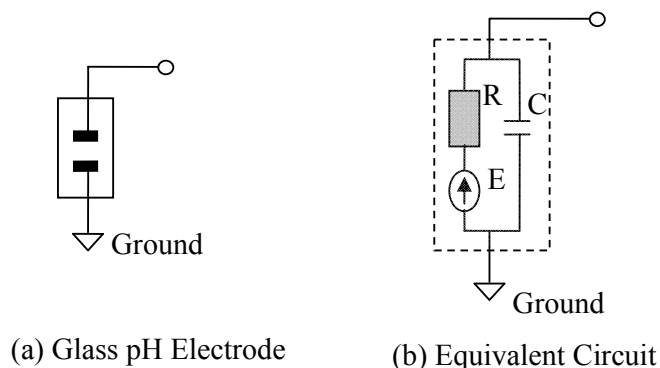


Figure 1. An equivalent circuit for the glass pH electrode.

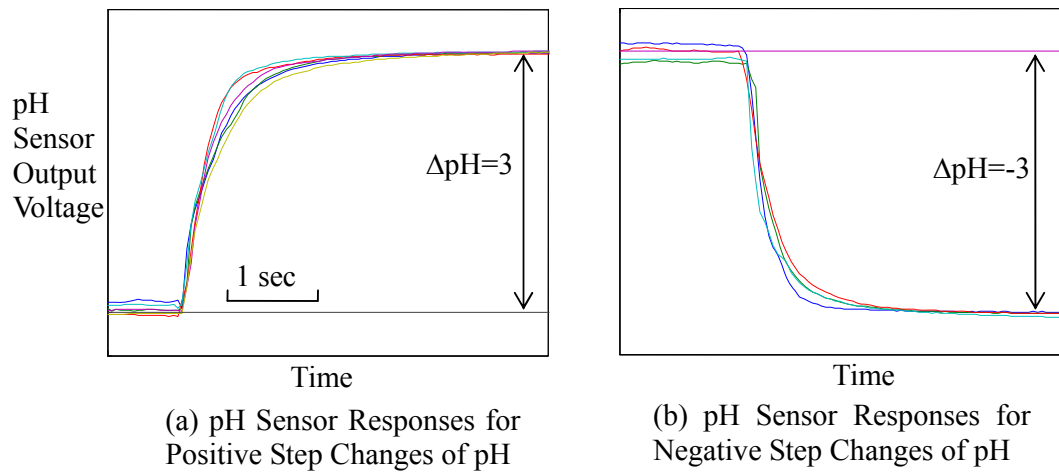


Figure 2. Responses of step changes in solution pH (Experimental results).

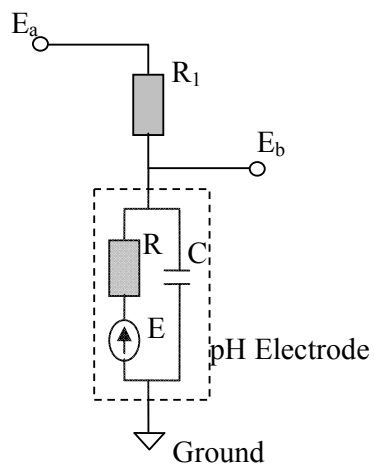


Figure 3. A model for the external voltage forcing.

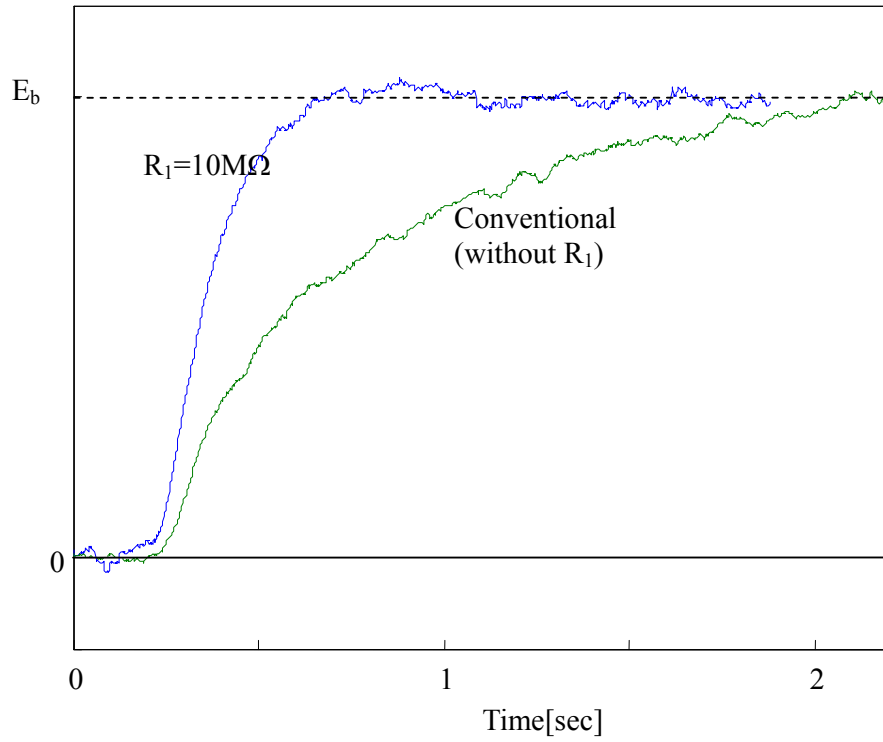


Figure 4. Responses of step changes in solution pH (Experimental results).

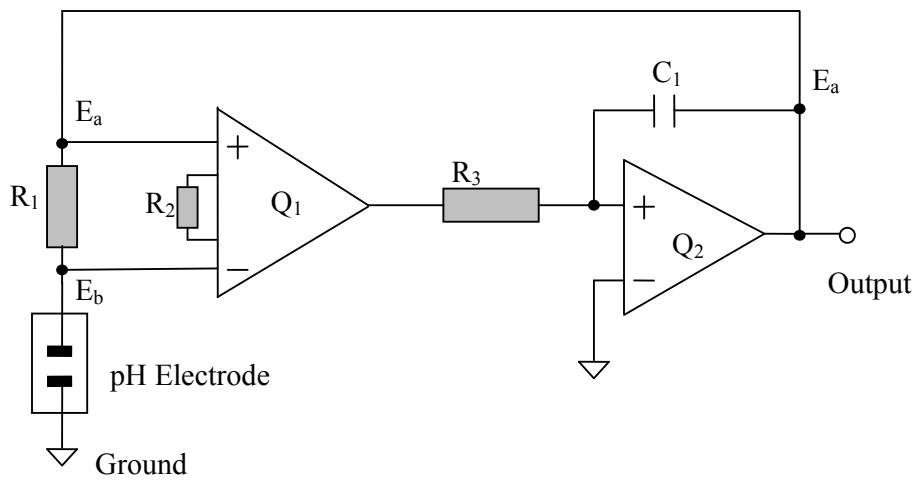


Figure 5. A proposed circuit for improved transient response of the glass pH electrode.