Slow drift modeling and compensation in the glass electrode dynamics for the fast measurement of pH

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Abstract−Glass electrodes for measuring pH in solutions show relatively fast responses with slow drifts. To design compensators to remove the drifts that hinder fast measurements of pH, a dynamic model that consists of ordinary and partial differential equations is proposed. It can explain such two-time scale responses of glass electrodes. The fitting accuracies of the proposed model are experimentally evaluated in frequency-domain and time-domain. The frequency responses obtained from the square wave responses show the fitting abilities of the proposed model, and the step responses also support this. The step responses filtered based on the proposed model show that pH measurements can be made considerably faster. The proposed model can be used to improve the dynamics of glass pH electrodes by compensating dynamic elements causing slow drifts.

Key words: Glass Electrode, pH Sensor, Slow Sensor Drift, Identification, Dynamic Compensation

INTRODUCTION

Since Cremer [1] reported the pH response of oxide glasses in 1906, glass electrodes have long been used for measuring the hydrogen ion concentrations in solutions. Recently, many techniques including semiconductor and optical sensors have been available [2,3]. These sensors are small and comparatively cheap, and can be used as disposable sensors [3]. In spite of these developments, the glass electrode is still of great practical importance for measuring the hydrogen ion concentration. The glass electrode is stable mechanically and chemically, and can be used in various solutions including turbid media. It is comparatively easy to handle, not requiring any special pretreatment of the solutions. It is relatively fast and can be used for on-line measurements. Many experimental and theoretical studies for the origin of pH-glass electrode potential have been presented. However, the origin of the glass electrode potential is still controversial. In some theoretical approaches, the potential is attributed to the surface properties of the glass and, in others, to its permeability properties. It is shown that hydrogen ions do not cross the glass membrane by experiments [4] and this assumption has been widely accepted [5]. On the other hand, some researchers have argued against the assertion that hydrogen ions in glass are immobile [6].

The pH-glass electrode shows a fast response with a slow drift [7]. The slow drift hinders the fast measurement of pH and becomes a bottleneck for some equipment requiring fast operation such as the autotitrator [8]. When an accurate dynamic model is available, the slow drift can be compensated. For this, empirical models of first order [8] and second order [9] have been presented. Here, a physico-chemical model for the pH response of glass electrode is proposed. While the time constant for the fast response is an order of second, that for the slow drift can be an order of ten seconds and cause trouble in measuring pH fast. To explain this two time-scale responses, more complicated models where the glass membrane is assumed to be divided into dry and hydrated regions have been presented recently [10]. Here, based on the previous theoretical studies, a dynamic model is proposed and its validity is tested with experiments. Methods to identify model parameters and to compensate dynamics for faster responses are suggested.

DYNAMIC MODEL OF THE pH-GLASS ELECTRODE

Fig. 1 shows a typical glass pH sensor module. The lower bulb in the sensor module consists of the pH-sensitive glass. Inside the bulb, there is a buffer solution with a known hydrogen ion concentration. The hydrogen ion concentration in the outside solution is
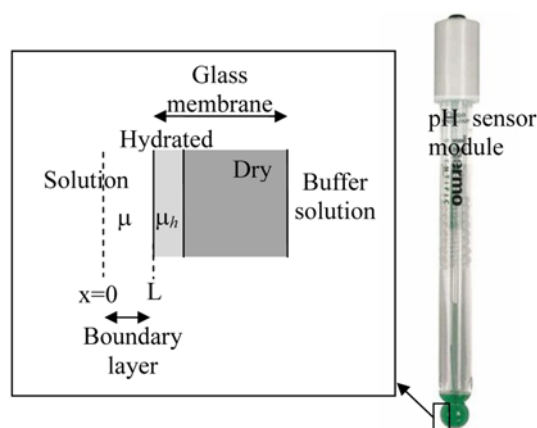

Fig. 1. A typical pH sensor module and a modeling scheme of the pH sensitive glass membrane.

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measured through the electric potential difference between both sides of the glass membrane. The hydrogen ion will diffuse and adsorb to the glass membrane surface. By the Nernst equation [2], the potential of this glass electrode becomes

$$E=E_0-0.059\log_{10}[H^+]=E_0+0.059\times pH \tag{1}$$

where $[H^+]$ is the molar concentration of hydrogen ion in the outside solution and $pH=-\log_{10}[H^+]$. Because the hydrogen ion concentration of the inside buffer solution is constant, the potential difference will represent the hydrogen ion concentration of the outside solution.

The glass electrode potential shows dynamics for changes in the solution pH. A source that will contribute to the dynamics of the glass electrode is the diffusion through the boundary layer between the solution and the glass surface. It is relatively fast and can be modeled with a partial differential equation. Besides this relatively fast response, there is a slow drift. For the slow drift in the pH response, the concept of the hydrated region in the glass membrane where the mobile hydrogen ion can permeate has been introduced ([6], [10] and [11]). The length of the hydrated region is several micro meters and it can be considered as a first-order lumped system. Here, we adopt this model that consists of the partial differential equation and a first order ordinary differential equation. Fig. 1 shows the schematic diagram for our dynamic model. We assume that the driving force for diffusion and permeation is the electric potential and equations can be derived for the chemical potential of [12]

$$\mu=\mu_0+RT\ln[H^+] \tag{2}$$

The pH responses show similar dynamics regardless of the pH values, and this cannot be obtained with dynamic equations linear for the hydrogen ion. For this, we use the quantity of Eq. (2), which is equivalent to the pH value. Diffusion and permeation equations are

$$\frac{\partial\mu}{\partial t}=\alpha\frac{\partial^2\mu}{\partial x^2} \tag{3}$$

$$\tau_h\frac{d\mu_h}{dt}=\mu(1,t)-\mu_h \tag{4}$$

where $\mu(x, t)$ is the chemical potential of the hydrogen ion in the boundary layer of solution, $\mu_h(t)$ is the chemical potential of the hydrogen ion in the hydrated region of the glass membrane, x is the distance variable in the boundary layer normalized by the boundary layer length L and t is the time variable.

The boundary conditions for Eq. (3) are

$$\mu(0, t)=u(t) \tag{5}$$

$$\frac{\partial\mu(1,t)}{\partial x}=-\beta(\mu(1,t)-\mu_h(t)) \tag{6}$$

where u(t) is the chemical potential of the hydrogen ion in the solution representing the change of pH. The chemical potential difference between the surface of glass membrane and the hydrated region is the driving force for the hydrogen ion permeation, and the constant β in Eq. (6) is its proportional constant. The constant α in Eq. (3) is the diffusivity over the square of boundary length L and the constant τ_h in Eq. (4) is the time constant of the hydrated region dynamics. The output variable representing the sensor signal is

$$y(t)=\mu(1, t) \tag{7}$$

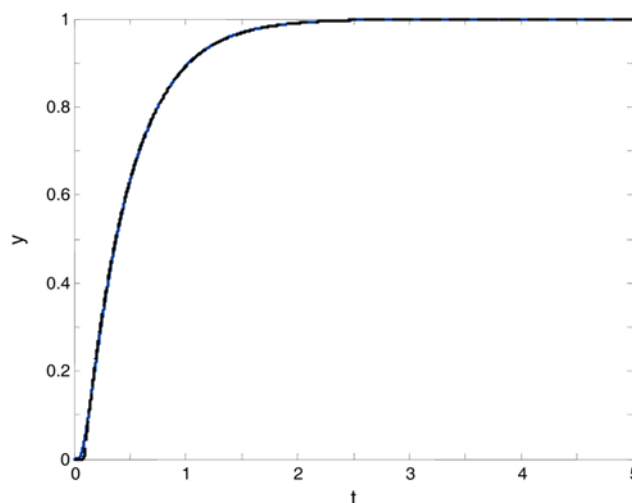
Fig. 2. Step responses of $G_a(s)=1/\cosh(\sqrt{s})$ (solid line) and its approximation $G_a(s)\approx\exp(-0.09s)/(0.41s+1)$ (dashed line).

The Laplace transform [13] is applied to Eqs. (3) to (7). It is easy to find the transfer function between y(t) and u(t), $Y(s)=G(s)U(s)$;

$$G(s)=\frac{2}{(1+Q)e^{\sqrt{s/\alpha}}+(1-Q)e^{-\sqrt{s/\alpha}}},\quad Q=\beta\frac{\tau_h\sqrt{\alpha}\sqrt{s}}{\tau_h s+1}$$

$$=\frac{1}{\cosh(\sqrt{s/\alpha})}\frac{1}{1+\frac{\beta\tau_h s}{\tau_h s+1}\frac{\tanh(\sqrt{s/\alpha})}{\sqrt{s/\alpha}}} \tag{8}$$

The system is infinite dimensional and, for a practical application, the transfer function of Eq. (8) should be approximated.

First, the former part in G(s) is considered. The step response for $G_a(s)=1/\cosh(\sqrt{s/\alpha})$, shown in Fig. 2, can be approximated as

$$G_a(s)=\frac{1}{\cosh\left(\sqrt{\frac{s}{\alpha}}\right)}\approx\frac{\exp\left(-\frac{0.09}{\alpha}s\right)}{\frac{0.41}{\alpha}s+1} \tag{9}$$

The dead time and first-order lag are consistent with physical phenomena of the hydrogen ion travelling by diffusion. This term will represent the fast part of glass electrode dynamics.

The constant β is less than 0.1 and the constant τ_h is much larger than the time constant of $G_a(s)$. In this case, the terms of $\tanh(\sqrt{s/\alpha})/\sqrt{s/\alpha}$ in Eq. (8) can also be set to 1 [14];

$$G_b(s)=\frac{1}{1+\frac{\beta\tau_h s}{\tau_h s+1}\frac{\tanh(\sqrt{s/\alpha})}{\sqrt{s/\alpha}}}\approx\frac{1}{1+\frac{\beta\tau_h s}{\tau_h s+1}}=\frac{\tau_h s+1}{\tau_h(1+\beta)s+1} \tag{10}$$

This lead/lag module can explain the slow drift of glass electrode dynamics.

The final transfer function is

$$G_m(s)=\frac{\exp\left(-\frac{0.09}{\alpha}s\right)}{\frac{0.41}{\alpha}s+1}\frac{\tau_h s+1}{\tau_h(1+\beta)s+1}\approx G_a(s)G_b(s) \tag{11}$$

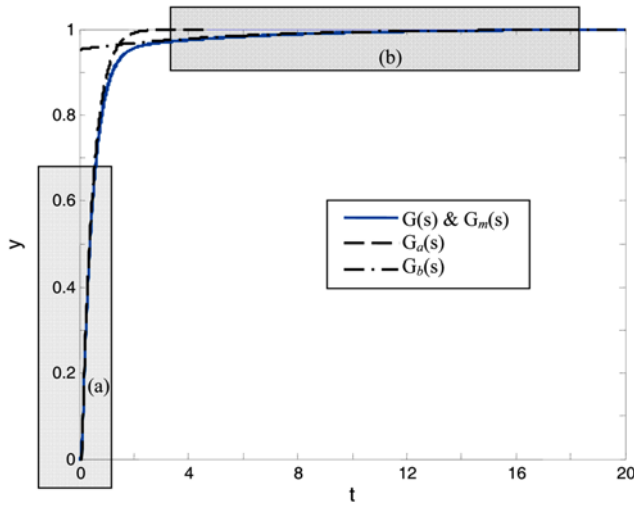Fig. 3 illustrates the proposed model of Eq. (8) and its approxima-

Fig. 3. Step responses for the proposed model with $\alpha=1$, $\tau_h=5$, and $\beta=0.05$.

tion of Eq. (11).

SIMPLIFIED IDENTIFICATION OF MODEL PARAMETERS

The proposed model of Eq. (11) has three parameters. Here a simplified method to find the model parameters from a step response is described. As shown in Fig. 3, when the time constant of $G_b(s)$ is much larger than that of $G_a(s)$, we can identify the model parameters independently. For $G_a(s)$, the initial part of step response (**A** in Fig. 3) is [15,16]

$$y_a(t) = 1 - \exp\left(-\left(t - \frac{0.09}{\alpha}\right)\Big/\left(\frac{0.41}{\alpha}\right)\right), \quad t > 0.09/\alpha \tag{12}$$

Rearranging Eq. (12), we have, for $t > 0.09/\alpha$,

$$\ln(1 - y_a(t)) = \frac{0.09}{0.41} - \frac{\alpha}{0.41}t \tag{13}$$

This equation is linear [17] for t and the parameter α can be obtained from the slope in the plot of $\ln(1-y_a(t))$ versus t. This identification problem is a famous one and can be found in many control textbooks [15,16].

For $G_b(s)$, the final part of step response (**B** in Fig. 3) is used. Since

$$G_b(s) = \frac{\tau_h s + 1}{\tau_h(1+\beta)s + 1} = \frac{1}{1+\beta} + \frac{\beta}{1+\beta}\frac{1}{\tau_h(1+\beta)s + 1} \tag{14}$$

we have

$$y_b(t) = 1 - \frac{\beta}{1+\beta}\exp\left(-\frac{t}{\tau_h(1+\beta)}\right) \tag{15}$$

For noise-free responses, the same technique as in Eq. (13) can be used. However, when the output y(t) is corrupted with noise, the value $(1-y_b(t))$ can be negative and its logarithm does not exist [17]. A different method should be used. Consider the integral [18],

$$y_{bi}(t) \equiv \int_t^{t_f}(1 - y_b(t))dt \tag{16}$$

Here t and t_f are the time span covering the region **B** in Fig. 3. The integral $y_{bi}(t)$ becomes

$$y_{bi}(t) = \frac{\beta}{1+\beta}\int_t^{t_f}\exp\left(-\frac{t}{\tau_h(1+\beta)}\right)dt$$

$$= \beta\tau_h\exp\left(-\frac{t_f}{\tau_h(1+\beta)}\right) + \beta\tau_h\exp\left(-\frac{t}{\tau_h(1+\beta)}\right)$$

$$= \beta\tau_h\exp\left(-\frac{t_f}{\tau_h(1+\beta)}\right) + \tau_h(1+\beta)(1-y(t)) \tag{17}$$

$$= \beta\tau_h\exp\left(-\frac{t_f}{\tau_h(1+\beta)}\right) + \tau_h(1+\beta) - \tau_h(1+\beta)y(t)$$

This equation is linear [17] for y(t) and the model parameter $\tau_h(1+\beta)$ can be obtained by linear regression between $y_{bi}(t)$ and y(t). When $\tau_h(1+\beta)$ is obtained, the linear regression method is applied to Eq. (15) for β. The parameter $\beta/(1+\beta)$ can be obtained for the linear regression between $y_b(t)$ and $\exp(-t/(\tau_h(1+\beta)))$ for the time covering the region **B** in Fig. 3.

EXPERIMENTS AND DISCUSSION

To illustrate the validity of the above model, several experiments are carried out. The potentials of glass electrode are amplified with the instrumentation amplifier INA101 (Texas Instrument). It has very high input impedance ($\sim10^{10}$ Ω) and hence measurements can be considered to be made under the zero current. The amplified signal is converted to the digital value with a lab-made data acquisition system that has a high resolution (16 bit) and low noise analog-to-digital (A/D) converter. The sampling time for the A/D conversion is set to 0.1sec. Glass electrodes used are PE03 (the Digital Instrument Co.) and Corning Cat. No. 476086.

1. Frequency Responses

For intuitions about the model structure of pH glass electrode, frequency responses are obtained. Since the sinusoidal inputs are hard to implement, square wave inputs are used. By applying the Fourier transformation to both input and output signals, frequency responses can be obtained easily. The experimental system is shown
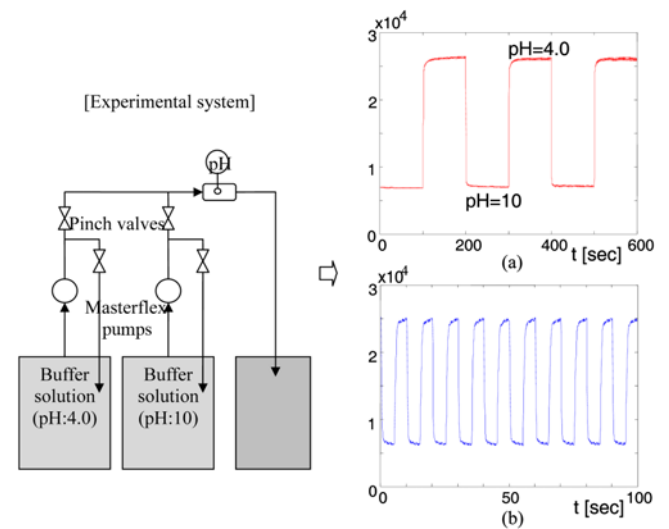

Fig. 4. Square wave responses with alternating buffer solutions of pH=4.0 and 10 whose periods are 200 sec (a) and 10 sec (b), respectively.

in Fig. 4. Two peristaltic pumps are pumping two buffer solutions with pH of 4.0 and 10. Four pinch values are switched to let two buffer solutions flow to the in-line pH measuring system alternatively. When one buffer solution flows to the in-line pH measuring system, the other buffer solution returns back to its tank. In this way, the buffer solutions are switched without their flow pattern changing much. Responses for the square wave inputs with various periods as shown in Fig. 4 are obtained. The square wave responses after they are settled to their cyclic steady states are analyzed. The frequency responses can be [15,16]

$$G(j\omega) = \frac{Y(j\omega)}{U(j\omega)} = \frac{\int_0^{nP} y(t)e^{j\omega t}dt}{\int_0^{nP} u(t)e^{j\omega t}dt}$$

$$= \frac{1}{\int_0^{nP} u(t)e^{j\omega t}dt}\left(\int_0^{nP} y(t)\cos(\omega t)dt + j\int_0^{nP} y(t)\sin(\omega t)dt\right) \quad (18)$$

$$= \frac{(2k+1)\pi}{nP\bar{u}}\left(\int_0^{nP} y(t)\cos(\omega t)dt + j\int_0^{nP} y(t)\sin(\omega t)dt\right),$$

$$\omega = (2k+1)2\pi/P, \quad k = 0,1,2,\cdots$$

where P is the period of square wave input, nP is the time span and $\bar{u}$ is the size of input.

Fig. 5 shows the normalized amplitude ratio of $|G(j\omega)|/G(0)$. We can see that the proposed model can fit the amplitude ratio well. The fitted model parameters for $G_m(s)$ are $\alpha = 1.23$, $\beta = 0.05$, and $\tau_h = 4.68$.

2. Step Responses

The pH responses for the step changes of hydrogen ion in solution are tested. For this, a simple experimental system as shown in Fig. 6 is assembled. In a 50 mL beaker, a small amount of water is stirred and its pH is being measured. When the pH of water remains constant, 50 mL of a buffer solution is poured quickly and the change of pH is recorded. The obtained pH responses are shown in Fig. 6. Since pH values of buffer solutions are not changed much even when
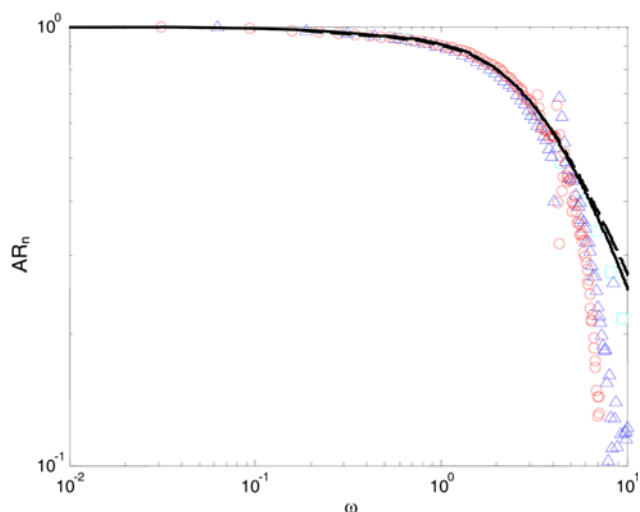
Fig. 5. Normalized amplitude ratios (ARₙ) obtained from the square wave responses with periods of 10 (cyan square), 100 (blue triangle) and 200 sec (red circle), and those of the proposed models of Eqs. (8) (solid line) and (11) (dashed line).
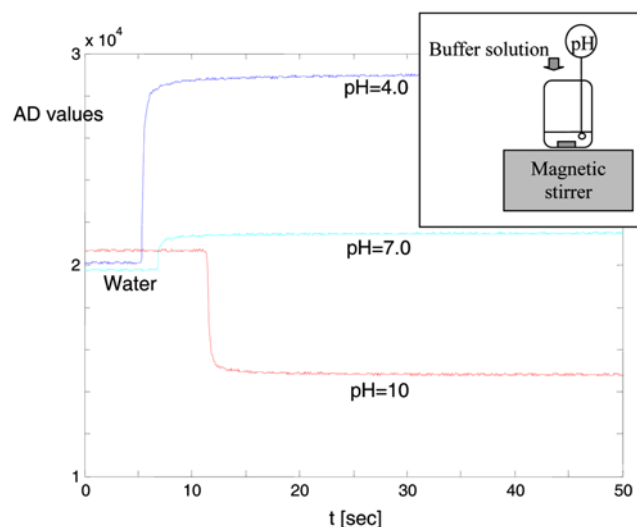
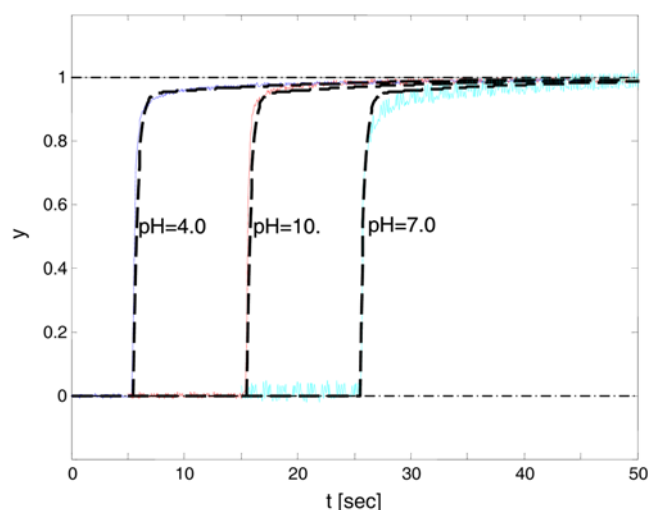**Fig. 6. Step responses obtained by adding buffer solutions of pH= 4.0, 7.0 and 10.**

Fig. 7. Normalized step responses, the proposed model responses (dashed lines; the model is IAE optimal for the step response with the buffer solution of pH=4.0).

they are diluted, the solution pH can be assumed to be changed abruptly. With the step response for the buffer solution of pH=4.0, model parameters are computed. For this, the Nelder and Mead method implemented in MATLAB (routine name is 'fminsearch') is used. For the fitting criterion, the integral of absolute errors (IAE) is used. Fig. 7 shows the normalized step responses and fitting results. The obtained model parameters are $\alpha = 1.1623$, $\beta = 0.0544$ and $\tau_h = 15.2321$. The step responses for the buffer solutions of pH=4.0 and pH=10 are very similar and our model can fit them very well. For the step response for the buffer solution of pH=7.0, the signal-to-noise ratio is high due to its smaller step change and the fitting accuracy is somewhat worse. Evidently, the usual first-order model cannot fit the step responses well.

The simplified identification method presented in the above section can be applied for faster identification of model parameters. The step response for the buffer solution of pH=4 is used. Model
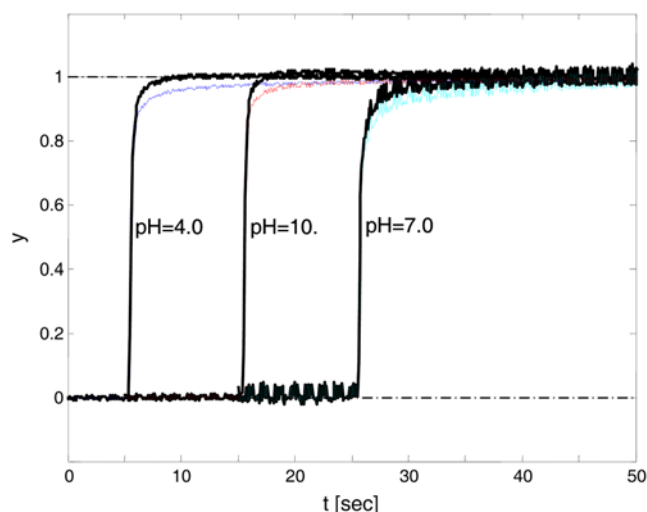
Fig. 8. Normalized step responses and their filtered responses (thick solid lines).

parameters obtained are α=0.9091, β=0.0424 and τ_h=15.6222. Since the sampling time is 0.1 sec, it will be hard to obtain α accurately. Other parameters of β and τ_h are very similar to those obtained through optimization. Model parameters obtained by the simplified identification method can be used as the initial values for the optimization.

3. Dynamic Compensation for a Faster Measurement of pH

The dynamics of a glass electrode may provide clues to the origin and mechanism of the glass electrode potential for the hydrogen ion concentration. Another practical usage of the proposed dynamic model is to remove the slow drift of glass electrode through a signal conditioning. Consider the lead-lag filter,

$$Y_f(s) = \frac{\tau_h(1+\beta)s+1}{\tau_h s+1} Y(s) \tag{19}$$

which is equivalent to the time-domain equation:

$$\dot{z}(t) = -\frac{1}{\tau_h} z(t) + \frac{1}{\tau_h} y(t)$$
$$y_f(t) = -\beta z(t) + (1+\beta) y(t) \tag{20}$$

This makes the pH response of glass electrode faster without changing its steady state performance (Fig. 8). Here the filter used for all three step changes is $Y_f(s)$=(16.06s+1)/(15.23s+1)Y(s). By implementing this filter, the filtered step responses ($y_f(t)$) reach their final steady states fast. Specifically, we can obtain the final pH values within 5 seconds. Otherwise, we may wait several 10 seconds until the pH values (y(t)) reach their new steady state values as shown in Fig. 8.

CONCLUSION

Glass electrodes are still used extensively to measure the hydro-

gen ion concentrations in solutions. They are relatively fast, but show slow drifts. For fast and accurate measurements of pH, the slow drift should be compensated. For this, a dynamic model that consists of ordinary and partial differential equations is derived. Its Laplace-domain solution and a simplified transfer function model are obtained. A method to find model parameters of the simplified transfer function model is given. To evaluate the fitting accuracies of the proposed models, square wave responses and step responses were obtained experimentally. Square wave responses provided frequency response data and showed that the proposed models are suitable to describe the glass electrode dynamics. Step responses also supported this. The proposed model can be used to improve the dynamics of the glass electrode. By applying a lead-lag module to compensate the slow drift, we can shorten considerably the time needed for the accurate measurement of pH.

REFERENCES

1. M. Cremer, *Z. Biol.*, **47**, 562 (1906).
2. A. S. Rad, M. Ardjmand, M. Jahanshahi and A. Safekordi, *Korean J. Chem. Eng.*, **29**, 1063 (2012).
3. D. C. Harris, *Exploring chemical analysis*, 4th Ed., Freeman & Company (2008).
4. G. Haugaard, *J. Phys. Chem.*, **45**, 148 (1941).
5. K. L. Cheng, *ACS Symp. Ser.*, **390**, 287 (1989).
6. Y. Abe and M. Maeda, *J. Electrochem. Soc.*, **147**, 787 (2000).
7. R. P. Buck, *J. Electroanal. Chem.*, **18**, 363 (1968).
8. J. Lee, T. H. Lee, S. Lee and D. R. Yang, *Korean J. Chem. Eng.*, **26**, 636 (2009).
9. D. R. Yang, S. Lee, S. W. Sung and J. Lee, *IEEE Sensors J.*, **9**, 1793 (2009).
10. H. H. Kohler, C. Haider and S. Woelki, *Adv. Colloid Interface Sci.*, **114-115**, 281 (2005).
11. G. T. Yu, *Chem. Phys. Lett.*, **384**, 124 (2004).
12. A. N. Gorban, H. P. Sargsyan and H. A. Wahab, *Math. Model. Nat. Phenom.*, **6**, 184 (2011).
13. E. Kreyszig, *Advanced engineering mathematics*, 10th Ed., Wiley, New York (2011).
14. J. Lee and D. H. Kim, *Chem. Eng. J.*, **173**, 644 (2011).
15. S. W. Sung, J. Lee and I. B. Lee, *Process Control, System Identification and PID Controllers*, Wiley (2009).
16. D. E. Seborg, T. F. Edgar and D. A. Mellichamp, *Process dynamics and control*, 2nd Ed., Wiley, New York (2003).
17. S. Ju, S. J. Kim, J. Byeon, D. Chun, S. W. Sung and J. Lee, *Korean Chem. Eng. Res.*, **46**, 949 (2008).
18. J. Lee and T. F. Edgar, *Chem. Eng. Sci.*, **65**, 2629 (2010).