

A simple solid-state pH electrode based on Ag/AgCl-Cu
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Abstract

The protonic sense materials have been screened from our laboratory for development to microprobe electrodes. The basic measurement was based on potentiometric method using reference electrode and indicating electrode. The materials tested were aluminum-copper, platinum-carbon, silver/silver chloride-carbon, silver/silver chloride-copper and silver-aluminum. The potential measurement in mV unit of test solutions with various pH found that at least one proton contains 59 mV/pH range. The selectivity of materials to proton can be seen from the graph plotted between pH and mV count. The commercial glass electrode was used as comparing electrode and it showed the linear equation of $y = -58.00x + 392.1$ with $r^2 = 0.999$. The silver/silver chloride-copper probe was found to be the protonic sense material which provided linear equation of $y = -25.07x - 73.69$ with $r^2 = 0.931$. The selected solid-state pH electrode was applied to use as pH sensor for monitoring of pH of natural water collected between February and April, 2009. Data were analyzed statistically using Student's *t*-test and it was found that the results obtained from both pH meter coupled with the selected solid-state pH electrode are not significant different at 95 % confidence levels.

Keywords: solid-state pH electrode; miniaturization; protonic sense

INTRODUCTION

Electrochemical measurements for analytical purposes can be carried out under conditions of equilibrium (zero current) with potentiometric sensors or outside equilibrium (passage of current) with amperometric or voltammetric sensors (Brett and Brett, 1994) There are two types of potentiometry:(1) faradaic potentiometry based on well-known redox reactions; and (2) non-faradaic potentiometry based on ion or charge adsorptions onto a dielectric or semiconductor that can hold the charges (Cheng, 2002). Potentiometry entails not only measuring pH and redox potentials but also working with ion selective electrodes (ISE).Redox potentials can be measured with noble metal electrodes (all solid-state sensors) but other tasks often involve using sensors filled with liquids (Vonau *et al.*, 2005). pH measurement is one type of non-faradaic potentiometry which normally utilizes glass membrane sensor as an indicator electrode. However, glass membrane pH electrode is liable to be broken, difficult to miniaturized and cannot meet the increasing demand for the miniaturization of pH meter. Therefore, an alternative solid-state pH sensor (pH

sensing and reference electrodes) is currently of interest. Commercially available solid-state pH electrodes are mainly built around Ion Selective Field Effect Transistors (ISFETs). For example, the pH-sensitive ISFETs system developed by Sentron, Inc. (Gig Harbor, WA) uses a solid-state silicon dioxide transistor with an aluminum oxide gate that selectively interacts with protons and detects a change in current which corresponds to pH (Poller *et al.*, 1998). These sensors have demonstrated to be stable, robust and reliable for pH measurements in the laboratory. However, their performance in field conditions and complex samples is still to be determined (Jimenez *et al.*, 2003). During the last decade, researcher have been published for pH determination using many other efficient solid-state pH sensors including polymer film modified electrode (Zhang *et al.*, 2002; Yuan *et al.*, 1993; Zhao *et al.*, 1999; Kinlen *et al.*, 1994), sol-gel technology based pH sensors (Li *et al.*, 2002; Makote and Collinson, 1999; Butler *et al.*, 1998), screen-printed ruthenium dioxide electrode (Koncki and Mascini, 1997), fiber optic pH sensor (Khan *et al.*, 2009) and LED based solid-state pH sensor (Lau *et al.*, 2006). Furthermore, metal/metal oxide pH sensors (Yamamoto *et al.*, 2003; Wang *et al.*, 2002; Qingwen *et al.*, 2000; Li *et al.*, 2006) received more interest with its excellent characteristics of easy miniaturization, a long life time and a strong tip which make miniaturization of pH meter possible. Therefore, this research aimed to design and fabricate a simple Ag/AgCl-Cu solid-state pH electrode for coupling with a miniaturized laboratory-made pH meter to use as a field-trip equipment.

EXPERIMENTAL PROCEDURE

Materials and Methods

Materials

All chemicals used were of analytical grade and all solutions were prepared by using deionized water (The Elgastat Maxima-HPLC equipped with Option 3B, ELGA, England). The acid solutions were prepared from hydrochloric acid (37%, Merck, Germany); pH 2 and 3. The base solutions were prepared from sodium hydroxide (99%, Merck, Germany); pH 11 and 12 and sodium hydrogen carbonate (Merck, Germany); pH 8-10. Acetate buffer solutions (pH 4-6) were prepared from 0.1 M sodium acetate and 0.1 M acetic acid. The dynamic range of this method is about pH 2.0-12.0 which either 1.0 M hydrochloric acid or 1.0 M sodium hydroxide was added drop wise to obtain the desired pH value.

Screening of materials to be solid-state pH electrode

Ag wire (60 mm length, 0.25 mm diameter, 99.9%, Aldrich, Germany) was dipped in 0.6 M FeCl₃ for one night to form a Ag/AgCl reference electrode. The Ag/AgCl wire was then soldered with the cable followed by inserted into a glass capillary (75 mm length, 2 mm diameter) as shown in Figure 1. Ag wire (60 mm length, 0.25 mm diameter, 99.9%, Aldrich, Germany), Al wire (60 mm length, 1.0 mm diameter, 99.9%, Aldrich, Germany), Carbon (2H pencil lead, 60 mm length, 0.5 mm diameter, Steadler, Germany), Cu wire (60 mm length, 0.5 mm diameter, 99.9%, Aldrich, Germany) and Pt wires (60 mm length, 0.25 diameter, 99.9%, Aldrich, Germany) were tested as working and reference electrode. Each metal were

soldered with the cable then inserted into a glass capillary. The mV count of the test solutions (pH 2.0-12.0) were recorded using a commercial pH glass electrode (Horiba, Japan) and also the selected couple of metal and/or metal/metal oxide pH electrode coupled with the pH meter (Horiba pH meter F-21, Japan).

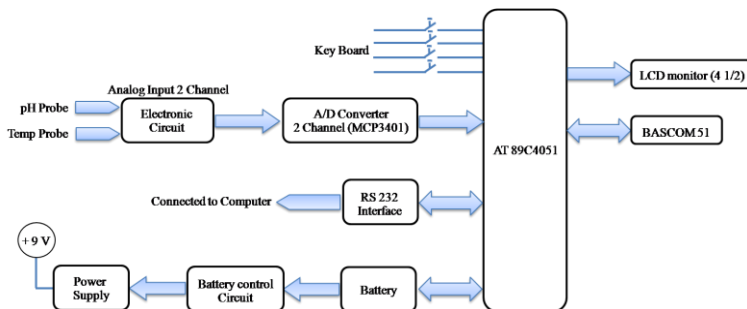


Figure 1 Block diagram of laboratory-made pH meter hardware.

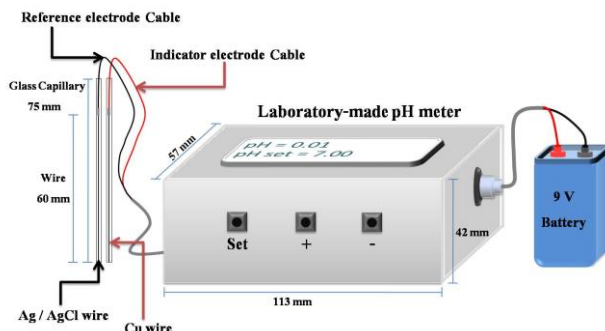


Figure 2 Schematic drawing of a laboratory-made solid-state pH measurement (NU3-pH meter).

Construction of laboratory-made pH meter

A laboratory-made pH meter was designed and fabricated using the AT89C4051 Microcontroller coupled with MCP3401 12-bit A/D converter used as data acquisition unit (Predko, 1999) to receive the potential signal from Ag/AgCl-Cu solid-state pH electrode. A block diagram of laboratory-made pH meter hardware as shown in Figure 1 was controlled by NU3-pH firmware (Masawat *et al.*, 2008). BASCOM51 compiler is used to create the microprocessor routine and programmed to its memory. The NU3-pH Firmware drives the A/D unit to convert analog potential of Ag/AgCl-Cu solid-state pH electrode to a digital format. Then, it converts potential to concentration of hydrogen ion (H^+) using Nernst's equation. The complete working unit (57 x 113 x 42 mm) is shown in Figure 2.

RESULTS AND DISCUSSION

Calibration curve of the solid-state pH electrode

The pH sensing performance of the selected solid-state electrode was tested in various pH solutions. It was found that the graphs plotted between pH and mV count of Al-Cu, Pt-C, Ag/AgCl-C and Ag-Al (Reference-Indicating electrode) were not linear except the Ag/AgCl-Cu that showed linear response as shown in Figure 3. It proves that the Ag/AgCl-Cu solid-state pH sensor has a sub-Nernstian response with slope of -25.1 mV/pH unit. Linear pH responses are obtained over a wide pH range of 2.0-12.0 ($r^2 = 0.931$).

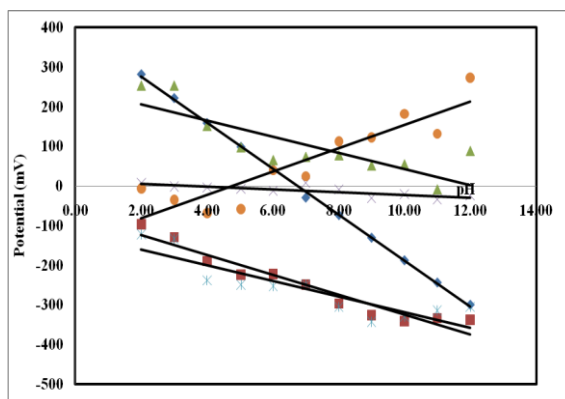


Figure 3 Potential responses with pH of commercial pH glass electrode comparing with solid-state pH sensors. ◆ Glass electrode ■ Ag/AgCl-Cu electrode ▲ Ag/AgCl-Pencil lead electrode × Ag-Al electrode * Al-Cu electrode ● Pt-Pencil lead electrode

Conditioning of the solid-state pH electrode

A Ag/AgCl wire (reference electrode) prepared was left in air (in dark), in distilled water and in 3 M KCl under same duration of time and their responses to hydrogen ion were measured coupled with Cu wire (indicating electrode). It was found that the Ag/AgCl wire left in 3 M KCl and Cu wire (without any mechanical polish) provided the reproducible potential slope for all measurements. It can be assume that it forms CuO on the surface. Therefore, the possible response mechanism of Cu electrode could be acted as metal oxide electrodes, a non-stoichiometric composition and/or more active OH sites at the surface of metal oxide are responsible for the pH response behaviors of metal oxide electrodes (Qingwen, *et al.*, 2000).

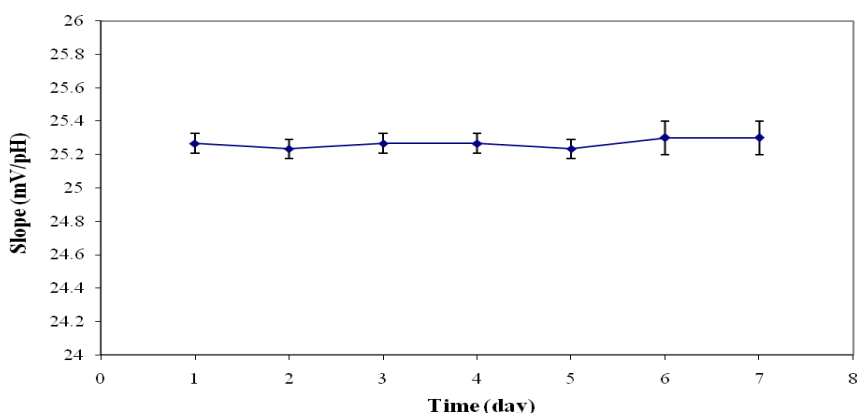


Figure 4 The stability test of Ag/AgCl-Cu solid-state pH electrode in test solutions (pH 2.0-12.0). Three replicates in each day.

Stability, reproducibility and lifetime of the solid-state pH electrode

The Ag/AgCl-Cu solid-state pH electrode was tested over a period of 7 days after fabrication and the results are shown in Figure 4. It displays that the slope of the calibration curve of the electrode has slightly variation during the period of 7 days. Moreover, when the solid-state pH electrode was coupled with the laboratory-made pH meter and used for pH monitoring of natural waters in the real situations, the relative standard deviations are less than 10% ($n=7$) in every places of natural water collected 3 times each month. This indicates that the Ag/AgCl-Cu solid state pH electrode is stable according to conditioning as describe above. The lifetime of the electrode was at least 6 months when it was used everyday without any mechanical problem developed

Selectivity of the solid-state pH electrode

The Ag/AgCl-Cu solid-state pH electrode was tested for selectivity with some monovalent and divalent anions and cations. The graphs plotted between potential reading of the Cl^- , K^+ , Na^+ , Cu^{2+} , Ca^{2+} , Zn^{2+} and Mg^{2+} at different concentration ($10^{-1} - 10^{-4}$ M) in the absent of hydrogen ion indicates that the Ag/AgCl-Cu electrode has excellent selectivity for Na^+ , Cu^{2+} and Zn^{2+} . The electrode could exhibit sub-Nernstian response with not only hydrogen ion but also with Na^+ , Cu^{2+} and Zn^{2+} as can be seen in Table 1. Although this seems that this electrode is not selective, fortunately, water samples were collected from the ornament pond which interference of Na^+ , Cu^{2+} , Zn^{2+} (and may be Cl^- and K^+) could be negligible because the concentration of these ions are very low.

Table 1 The response of Ag/AgCl-Cu electrode with some anions and cations.

Anions/Cations	Concentration range studies (M)	Slope (mV pM ⁻¹)	Linearity (r^2)
Cl ⁻	10 ⁻¹ – 10 ⁻⁴	-42.2	0.711
K ⁺	10 ⁻¹ – 10 ⁻⁴	-55.3	0.853
Na ⁺	10 ⁻¹ – 10 ⁻⁴	-27.7	0.997
Cu ²⁺	10 ⁻¹ – 10 ⁻⁴	-28.2	0.947
Ca ²⁺	10 ⁻¹ – 10 ⁻⁴	-5.30	0.118
Zn ²⁺	10 ⁻¹ – 10 ⁻⁴	-28.6	0.984
Mg ²⁺	10 ⁻¹ – 10 ⁻⁴	-6.90	0.193

Application to real samples

The Ag/AgCl-Cu solid-state pH electrode coupled with laboratory-made pH meter was applied to use for monitoring of pH of natural water collected from five places around Naresuan University, Phitsanulok Thailand; Reservoir, Nong Lek canal, King Naresuan pond, pond beside Faculty of Science and pond beside Supunkanlaya swimming pool, 10 points at each area, between February and April, 2009 and the results are shown in Table 2. The RSD in some places were a bit high but all less than 10%, therefore, the results were acceptable. It was found that the results obtained from Ag/AgCl-Cu solid-state pH sensor coupled with laboratory-made pH meter and commercial pH glass electrode coupled with commercial pH meter (Horiba, Japan) are not significant different at 95% confidence levels.

Table 2 Mean pH values of natural waters collected 10 points at each place when using Ag/AgCl-Cu solid state pH electrode coupled with laboratory-made pH meter comparing with glass electrode coupled with commercial pH meter.

Sources of Natural water	Mean pH values (%RSD) when using					
	Glass electrode coupled with commercial pH meter			Ag/AgCl-Cu solid state pH electrode coupled with lab-made pH meter		
	Feb.	Mar.	Apr.	Feb.	Mar.	Apr.
Reservoir	7.8 (7.0)	8.5 (3.5)	8.2 (2.1)	7.5 (9.2)	8.2 (3.0)	7.9 (0.7)
Nong Lek Canal	7.4 (6.7)	8.5 (0.9)	7.5 (1.3)	6.9 (9.8)	9.1 (8.3)	7.7 (4.1)
King Naresuan pond*	8.0 (1.3)	7.9 (1.2)	8.0 (3.8)	6.9 (5.7)	7.6 (6.1)	8.0 (7.1)
Pond beside Sci.Fac.*	6.8 (3.6)	7.2 (0.8)	7.4 (2.7)	7.0 (9.2)	7.0 (9.3)	7.0 (2.4)
Pond_beside	7.3 (4.7)	7.4 (2.5)	7.7 (1.0)	7.4 (8.6)	7.2 (7.0)	8.0 (8.7)
Supun.swimming pool*						
*ornament pond						

CONCLUSIONS

In this paper, a simple solid-state pH electrode based on Ag/AgCl-Cu was developed. The prepared electrode exhibits a wide pH range response of 2.0-12.0 as shown in Figure 3. Comparing with the commercial glass pH electrode, the preparation of the electrode is simple, not expensive and the lifetime is more than 6 months. Moreover, the Ag/AgCl-Cu solid-state pH electrode coupled with laboratory-made pH meter is convenient for applying to outdoor pH measurement.

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