KMUTNB Int J Appl Sci Technol, Vol. 9, No. 3, pp. 225–233, 2016

Research Article

Simple Solid-State Ag/AgCl Reference Electrode and Its Integration with Conducting Polypyrrole Electrode for the Production of All-Solid-State pH Sensor

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DOI: 10.14416/j.ijast.2016.05.001
Received: 23 March 2016; Accepted: 2 May 2016;

Abstract

In this work, a solid-state Ag/AgCl electrode was successfully fabricated via electrodeposition of silver, followed by chlorination in the presence of ferric chloride to obtain silver chloride. Stainless steel rod was used as the supporting electrode. XPS and SEM were performed on the surfaces of silver to investigate the changes in surface composition and morphology, revealing the successful formation of silver chloride on the silver layer after the chlorination process. Calibrated against the commercial Ag/AgCl electrode, the developed solid-state Ag/AgCl electrode showed insensitive potentiometric response in different buffer solutions with the response time of 10 s. All-solid-state pH sensor, constructed by integrating the solid-state Ag/AgCl electrode with the polypyrrole-based pH indicative electrode, showed a linear potentiometric sensitivity of –53.55±1.33 mV.pH^{-1} ($r^2 > 0.99$) over pH range of 2–12 with excellent reproducibility. The pH measurement in the selected real solutions was demonstrated, suggesting that the constructed all-solid-state pH sensor showed the comparable sensing performance to the commercial glass pH electrode. The all-solid-state sensor is currently miniaturized for the further use in microfluidics and flow injection analysis system.

Keywords: Ag/AgCl reference electrode, pH sensor, All-solid-state sensor, Polypyrrole, Potentiometric sensor

1 Introduction

Important function of a reference electrode in a potentiometric sensor is to provide constant potential that is stable with respect to the indicative electrode during electrochemical measurement. There are various kinds of reference electrodes including standard hydrogen electrode (SHE), saturated calomel (Hg/Hg_2Cl_2) electrode (SCE) and silver/silver chloride (Ag/AgCl) electrode. Nowadays, the Ag/AgCl electrodes are

Please cite this article as: W. Prissanaroon-Ouajai, P. J. Pigram, and A. Sirivat, "Simple solid-state Ag/AgCl reference electrode and its integration with conducting polypyrrole electrode for the production of all-solid-state pH sensor," *KMUTNB Int J Appl Sci Technol*, vol. 9, no. 3, pp. 225–233, July–Sept. 2016.

preferably applied in the potentiometric sensors because they are more convenient for use and their potential is stable and well defined in relation to the potential of SHE. In addition the Ag/AgCl electrodes exhibit miniaturization possibilities and non-toxicity [1], [2]. However, the conventional Ag/AgCl electrodes exhibit major drawbacks of their liquid electrolyte filling and being mechanical fragile, limiting the further miniaturization for *in vivo* studies or application at high pressure and temperature.

Solid-state reference electrodes (SSREs), have been extensively developed to overcome these drawbacks by eliminating the need of an internal filling solution. SSREs serves as pseudo-reference electrodes because they do not maintain a constant potential but vary predictably with conditions. SSREs have attracted huge attention due to its simplicity, easy maintenance, no liquid junction potential and no contamination of the test solution by solvent molecules or ions that a conventional reference electrode might transfer. In addition, SSREs offer possibilities for mass production and miniaturization [3].

There are several ways to fabricate the thin film Ag/AgCl pseudo-reference electrodes including electrochemical deposition [4], [5], sputtering [6], [7] and screen printing [8], [9]. The screen printing technique is simple and low cost but it is not reproducible. The elctrodeposited Ag layer and sputtered Ag layer can be converted to AgCl via an anodic oxidation and chlorination. The first process is usually performed by applying a fixed current to the Ag in presence of HCl solution [10], [11] whereas the chlorination involves chemical oxidation of the Ag layer in the presence of ferric chloride ($FeCl_3$) [6]–[8].

One of critical issues of the pseudo-reference electrode is potential stability over a range of tested conditions. Instability of the solid-state Ag/AgCl has basically attributed to dissolution of the very thin layer, normally in few nanometers, of sparingly soluble AgCl and the subsequently generated mixed potentials at the electrode/solution interface. Silver chloride has solubility product constant (K_{sp}) of 1.76×10^{-10} which implies that about 1.9 mg of AgCl will dissolve in a liter of water at 25°C [12]. Coating with gel or polymeric membrane is a simple method to reduce the dissolution rate of AgCl. For example, thick film technology has been applied to coat a silver wire with a mixture of Ag, AgCl and $(NH_4)_2CO_3$ in epoxy resin [13]. Many other reports have involved the protection Ag/AgCl layers with polymeric membranes, such as aromatic polyurethane [14] and Nafion [15], in order to diminish possible ionic interference on its potential. Electrolyte doped polymeric membranes, such as KCl-doped polyvinyl acetate, KCl-doped vinyl ester resin and NaCl-doped polyvinyl chloride, have also been applied for this purpose [16]. Layer-by-layer polymer coating has been carried out to prepare the solid-state Ag/AgCl reference electrode by coating silicone rubber containing KCl on an AgCl surface, followed by a perfluorinated ionomer film and polyurethane based membrane [14]. Recently, graphene oxide has been used as a protective layer to coat a solid-state thin film Ag/AgCl electrode [6], leading to interlocked layered structures with good mechanical strength. Although stability of the solid-state Ag/AgCl reference electrodes developed from the literatures mentioned above was improved, new problem of response time has come up. The polymeric coatings create a diffusion barrier at electrode/solution interface, leading to long response time of the reference electrode, hence response time of the integrated sensors. Moreover, most of above fabrications turn out to be complicated and economically prohibitive since multi-step fabrication and expensive supporting electrodes, such as platinum, gold and silver, have been required.

In the present study, the solid-state Ag/AgCl electrode has been simply fabricated via an electrodeposition of Ag on a stainless steel rod followed by the chlorination of Ag in the presence of $FeCl_3$ to obtain solid-state Ag/AgCl electrode. In this case, $FeCl_3$ acts as an oxidizing agent and provides chloride ions. Stainless steel has been utilized here because it is cheaper than other conventional electrodes. In addition, stainless steel is less reactive than steel and aluminium, therefore, the electrodeposition of metallic silver can be achieved without pretreatment. The electrodeposited Ag forms a quasi-bulk phase, which allows subsequent formation of thick layer of AgCl [4]. Surface chemistry and morphology of Ag/AgCl electrode have been characterized by X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM), respectively. Possibility of the developed Ag/AgCl electrode for the practical use as a pseudo-reference electrode was investigated. All-solid-state pH sensor was constructed by integration the developed solid-state Ag/AgCl electrode with the polypyrrole-based pH indicative electrode (PPy-pH electrode), previously developed by the authors [17], [18]. Although preparations of solid-state Ag/AgCl electrode have extensively been developed [13]–[16], novelty of the present work is simple and cost-effective fabrication and integration of the solid-state Ag/AgCl electrode with the conducting polymer-based pH electrode to build an-all-solid state pH sensor. Sensing performance of the all-solid-state pH sensor has been investigated by potentiometric technique to verify the possibility of the sensor for the use in various applications, especially in flow cell analysis and microfluidic system.

2 Experimental Section

2.1 *Materials and chemicals*

Supporting electrodes in the present work were made of stainless steel rods (grade 430) fitted into Teflon tubes leaving the active area of 0.078 cm^2. The electrodes were mechanically polished thoroughly with alumina, rinsed with deionized water and subsequently cleaned by ultrasonic agitation for 5 min in deionized water before used. All chemicals used were in analytical grade and used as received. All solutions were prepared in deionized water (resistivity of 18.2 MΩ.cm). Silver nitrate ($AgNO_3$) and potassium chloride (KCl) were purchased from Fisher Scientific (UK) whereas ferric chloride ($FeCl_3$) was supplied from Fluka (Switzerland). Standard buffer solutions of different pH values were prepared with appropriate mixtures of citric acid ($C_6H_8O_7$) and boric acid (H_3BO_3) obtained from Merck (Germany), and Tri-sodium orthophosphate ($Na_3PO_4 \cdot 12\ H_2O$) obtained from Sigma–Aldrich (Germany) [19].

2.2 *Fabrication of solid-state Ag/AgCl electrode*

Silver has been electrodeposited on the stainless steel supporting electrode in 1 M $AgNO_3$ by using a three-electrode cell at room temperature (28°C). Another stainless steel electrode was used as an auxiliary electrode while a commercial Ag/AgCl electrode was served as a reference electrode. Firstly, an oxidative pretreatment was applied at a constant potential of +1.0 V for 30 s to remove any microscopic gas bubbles on the electrode surface. A constant potential of 1.5 V was subsequently applied to the cell for 30 minutes. The electrode surface was covered with silvery layer as shown in Figure 1(a).

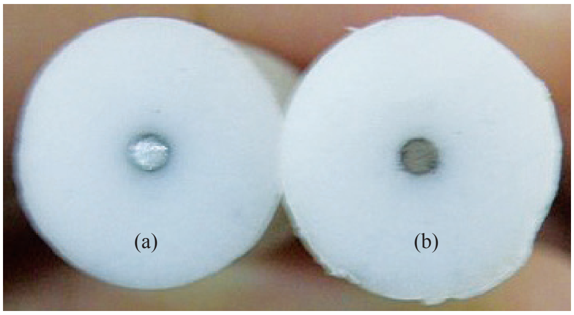

Figure 1: (a) As-electrodeposited Ag layer and (b) Ag layer after chlorination process.

Formation of AgCl was achieved by chemical oxidation of the Ag-coated electrode in an aqueous solution of 10 mM FeCl3. A small amount of 0.2 M HCl was added into the solution in order to avoid the hydrolysis of Fe^{3+}. The silver-coated electrode was immersed in the mixed solution and the reaction was allowed to take place for 10 s, leading to the coverage of AgCl on the electrode as seen in Figure 1(b). Leaving the reaction time for too long leads to very thin layer of the underneath Ag since most Ag is converted to non-adherent AgCl layer.

2.3 *Characterization of the Ag layers before and after chlorination*

Surface composition and morphology of the electrodeposited Ag layer on the stainless steel were investigated by various techniques to confirm the formation of AgCl after the chlorination in the presence of $FeCl_3$. Surface chemistry was investigated by XPS using an Axis Ultra DLD (Kratos, UK). The X-ray source was run with a monochromatised Al Kα radiation source (hν = 1486.6 eV) at 150 W. Survey and high resolution region spectra were recorded using 160 eV and 20 eV analyzer pass energies, respectively. Spectra were quantified using CasaXPS software (version 2.0.37, Casa Software Ltd., UK). Morphology was examined with a JSM-6480LV SEM (JEOL, Japan) operated at an acceleration voltage of 15 kV. The samples were mounted on aluminium stubs using doubled side tape. Prior to analysis, the samples were coated with a thin platinum layer in a sputter coater under vacuum in order to reduce surface charging effects. The microscope chamber was maintained at a pressure $<10^{-4}$ Pa.

2.4 *Potentiometric performance of the solid-state Ag/AgCl electrode*

Since the solid-state Ag/AgCl electrode has been developed for the use as the reference electrode in production of an all-solid-state pH sensor, monitoring the effect of pH value on its potentiometric response is necessary. The open circuit potential (OCP) of all electrochemical cell was recorded against a commercial Ag/AgCl reference electrode, using a 2700 digital multimeter/data acquisition system (Keithley, USA) at room temperature (28°C). To estimate the response time of the solid-state Ag/AgCl electrode, the measurement was allowed to proceed until reaching the equilibrium in the phosphate buffer solutions with pH 4, 7 and 10 and the plot of potential versus time was constructed. The potential stability of the developed solid-state Ag/AgCl electrode was also studied in various pH values of phosphate buffer solutions.

2.5 *Construction and performance of all-solid-state pH sensor*

All-solid-state pH sensor has been constructed by integration of the solid-sate Ag/AgCl reference electrode with the PPy-pH electrode in one-compartment Teflon body as presented in Figure 2. Fabrication of the PPy-pH electrode has been described in our previous paper [18]. The conducting polypyrrole (PPy) was electropolymerized on the stainless steel rod in the presence of hydroquinone monosulfonate (HQS) as a functional dopant and oxalic acid. The PPy-pH electrode showed excellent sensitivity to different pH solutions with the linear potentiometric response [18]. Dimensions of the all-solid-sate pH sensor were 1.2 cm in diameter and 4 cm in height. To investigate the performance of the all-solid-sate pH sensor, the open circuit potential was recorded as a function of time in phosphate buffer solutions with different pH values and real solutions. A calibration curve was constructed by plotting open circuit potential (mV), against pH value of the solution. For comparison purpose, the separated commercial Ag/AgCl reference electrode and the PPy-based pH indicative electrode and a commercial glass pH electrode connected to a 510 pH meter (Eutech, US) were also used in the potentiometric measurements.

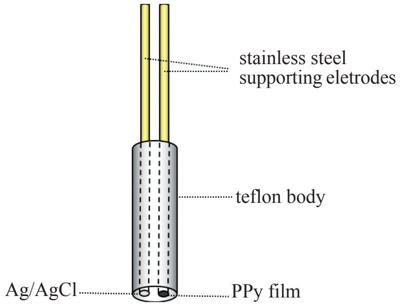

Figure 2: Construction of the all-solid-state pH sensor, consisting of the solid-state Ag/AgCl electrode and the PPy-indicative pH electrode.

3 Results and Discussion

Fabrication of the solid-state Ag/AgCl electrode developed in the present work simply involved two steps: electrodeposition of Ag on the stainless steel supporting electrode and subsequent chemical oxidation of Ag in the presence of chloride ions to form AgCl as the following reaction.

$$Ag + FeCl_3 \rightleftarrows AgCl + FeCl_2$$

Because AgCl has a very small solubility product constant (K_{sp}) of 1.76×10^{-10} at 25°C, the standard reduction potential of silver couples is reduced from 0.80 V (vs standard hydrogen electrode, SHE) for Ag^+/Ag to 0.223 V (vs SHE) for AgCl/Ag in the presence of chloride ions. On the other hand, the standard reduction potential of the redox couple of Fe^{3+}/Fe^{2+} keeps constant at 0.771 V (vs SHE) regardless of the concentration of Cl^- ions. The difference of the standard reduction potentials between AgCl/Ag and Fe^{3+}/Fe^{2+} couples provides the driving force for the reaction shown in above equation [20].

3.1 *Characterization of the Ag and AgCl layers*

XPS, the state-of-the-art surface characterization technique has been carried out to investigate the elemental composition and chemical state on the surface of the Ag layers before and after chlorination.

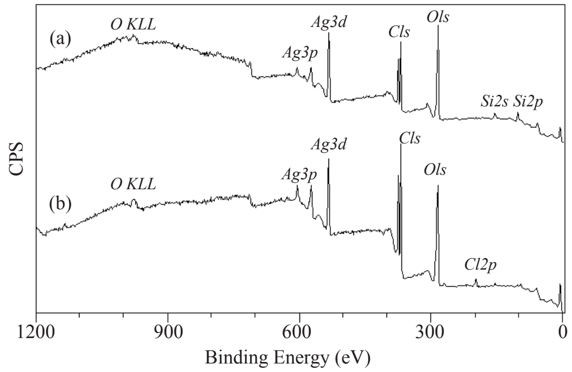

Figure 3: Survey XPS spectra of the Ag layers (a) before and (b) after chlorination in the presence of $FeCl_3$.

Figure 3 shows the XPS survey spectra for the surface of the electrodeposited Ag layers both before and after chlorination. The elemental atomic percentage, derived from the XPS survey spectra, is also shown in Table 1.

Table 1: Atomic percentages, derived from the XPS survey spectra, for the Ag layers before and after chlorination in the presence of $FeCl_3$

Surfaces of Ag Layer	O1s	Ag3d	C1s	Cl2p	Si2p
(a) before chlorination	22.5	14.9	56.4	-	6.2
(b) after chlorination	18.1	15.6	60.6	5.7	-

Figure 3(a) shows the survey XPS spectrum of the as-electrodeposited Ag layer, revealing the peaks for silver, oxygen, carbon and silicon. Those oxygen, carbon and silicon are basically attributed to some contamination and side effect during the electrodeposition process in ambient atmosphere. After chlorinated in the presence of $FeCl_3$, the additional signals of chlorine are observed [Figure 3(b)], suggesting the formation of AgCl layer on the Ag surface.

To demonstrate the chemical change on the surface of the electrodeposited Ag after chlorination, the high-resolution XPS spectra for of O1s, Cl2p and Ag3d were monitored, as presented in Figure 4. The high-resolution O1s spectrum of the as-electrodeposited Ag layer [Figure 4(a)] is divided into 3 peaks centered at 530.0 eV, 532.3 eV and 533.8 eV [21]. Two latter peaks are attributed to organic contamination absorbed on the silver surface whereas the first peak located at lower binding energy is associated with Ag-O. The content of Ag-O, estimated from the high-resolution O1s spectrum was found to be 4.3%. Since total silver content, derived from survey XPS spectrum was 14.9% (see Table 1), it suggested that the composition of the electrodeposited silver consisted of 6.3% metallic silver and 8.6% silver oxide in the form of Ag_2O. After the chlorination process, the Ag-O content on the electrode surface decreased significantly to 1.5% [Figure 4(d)].

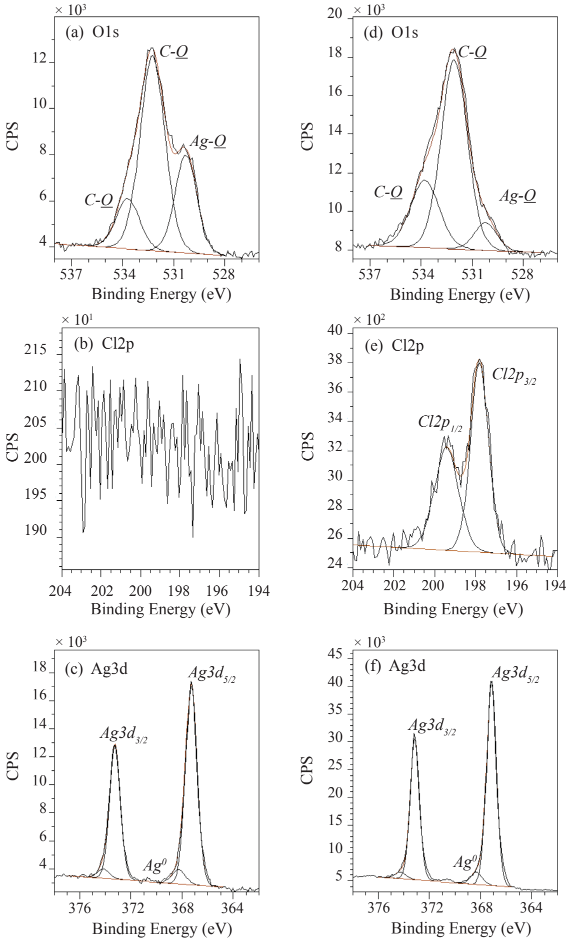

Figure 4: High resolution XPS spectra of O1s, Cl2p and Ag3d for the Ag layers (a)–(c) before and (d)–(f) after chlorination in the presence of $FeCl_3$.

In the case of Cl2p spectra, the signal of chlorine was observed only on the surface after chlorination [Figure 4(e)]. No Cl2p signal was found for the as-deposited Ag layer [Figure 4(b)]. The two peaks at 197.9 eV and 199.6 eV with a doublet separation of 1.7 eV in the Cl2p spectrum correspond to the binding energy of $Cl2p_{3/2}$ and $Cl2p_{1/2}$, respectively. According to the mole ratio of Ag and Cl in AgCl and the chlorine content reported in Table 1, it could be said that 5.7% AgCl has been formed after chlorination.

The high-resolution Ag3d spectrum for the as-electrodeposited silver shows the doublet peaks of Ag3d$_{5/2}$ and Ag3d$_{3/2}$ with the separation of 6.01 eV [Figure 4(c)]. The Ag3d spectrum could further divided into two different components at Ag3d$_{5/2}$ of 367.45 eV for silver oxide and 368.25 eV for the metallic silver (Ag^0) [22]. Similar shape of the Ag3d spectrum was observed for the Ag layer after chlorination [Figure 4(f)], however, the peak at lower binding energy of metallic silver seems to be smaller after chlorination. This observation corresponds well with the decrease in content of the metallic silver, derived from high-resolution Ag3d spectra, from 6.3% to 3.3% after chlorination. Information obtained from XPS clearly indicates the successful formation of AgCl on the electrodeposited Ag layer, creating the solid-state Ag/AgCl electrode which was further subjected to potentiometric measurements.

3.2 *Effects of pH on the potential of the solid-state Ag/AgCl electrode*

Reference electrode assembling in a pH sensor strongly requires a stable potential against any variations in pH value of the sample solution. Therefore, the developed solid-state Ag/AgCl electrode were subjected to the calibration of this property against a commercial standard Ag/AgCl electrode.

The open circuit cell potential of the solid-state Ag/AgCl electrode was monitored in buffer solutions with different pH values versus a commercial Ag/AgCl electrode with internal saturated KCl solution. Figure 5 shows that the solid-state Ag/AgCl electrode quickly reaches the equilibrium, where approximately 90% of the steady response occurs, within 10 s, showing the potential of 27±3 mV for all tested buffer solutions. Rough surface of the solid-state Ag/AgCl layer, as seen in Figure 6, probably is the reason for the fast response time. It is proposed that the rates of mass transport both to and from the electrode surface are significantly enhanced for rough surface compared with smooth surface [23]. Although, the cell potentials are greater the expected of near zero volt, the stability of the solid-state Ag/AgCl electrode seems to be unaffected by these potential errors. Compared to the as-electrodeposition in the buffer solution pH 7 showing unstable cell potential and greater offset potential about 80 mV (Figure 5), it is obviously that the AgCl formed after the chlorination process significantly improves the stability and performance of the solid-state Ag/AgCl as the reference electrode.

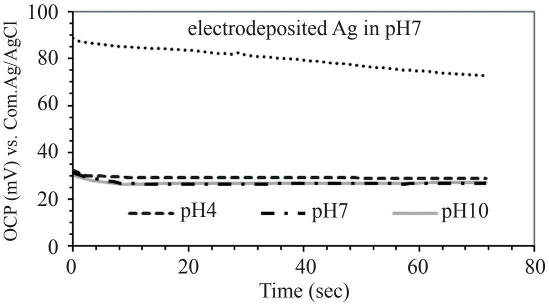

Figure 5: Open circuit potentials of the solid-state Ag/AgCl electrode vs. a commercial Ag/AgCl reference electrode recorded in the buffer solutions. The OCP of the as-electrodeposited silver in the buffer pH 7 was presented for comparison purpose.

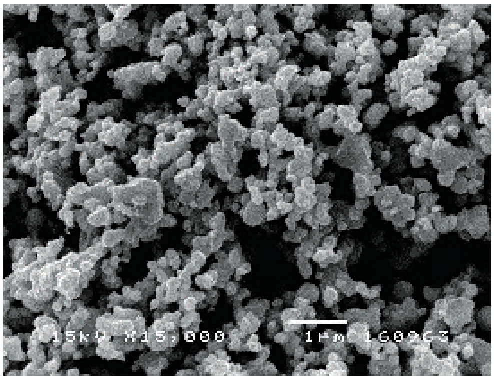

Figure 6: SEM image of the solid-state Ag/AgCl surface with the magnification of 15,000.

3.3 *Performance the solid-state Ag/AgCl as reference electrode in all-solid-state pH sensor*

All-solid-state pH sensor has been constructed by integration of the developed solid-sate Ag/AgCl electrode as the reference electrode with the PPy-pH electrode in one-compartment Teflon body (see Figure 2). Open circuit potentials of the all-solid-state pH sensor were recorded in different pH buffer solutions to investigate the performance of the solid-state Ag/AgCl as reference electrode. It is clearly seen from the

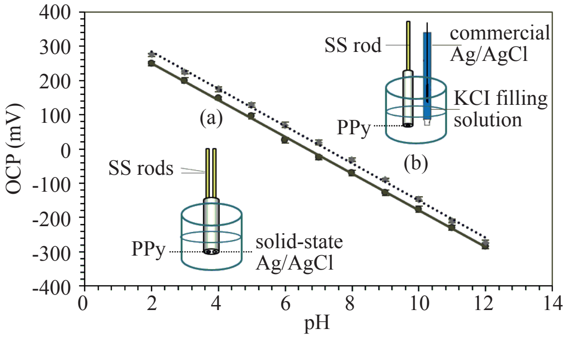

Figure 7: Calibration plots of the pH vs. cell potential of the PPy-sensitive pH electrode recorded against (a) solid-state Ag/AgCl reference electrode (solid line) and (b) commercial Ag/AgCl reference electrode (dash line).

calibration plot, shown in Figure 7(a), that all-solid-state pH sensor exhibited a near-Nernstian response slope of –53.55±1.33 mV.pH^{-1} with the linear regression correlation coefficient greater than 0.99 over the pH range of 2–12. Small potential deviation, derived from three independent electrodes, indicates the great reproducibility in the fabrication process of the all-solid-state pH sensor. The potentiometric response of the PPy-pH electrode when exposed to different pH solutions arises from the structural changes of both the electrically conducting PPy itself and the functional dopant as discussed in details previously [17]. For comparison purpose, the calibration plot of the pH sensor comprising of the PPy-pH electrode and separated commercial Ag/AgCl reference electrode is included in Figure 7(b), showing the response slope of –54.35±1.39 mV.pH^{-1}. Although the difference in open circuit cell potentials, approximately 23–30 mV, of these two constructed pH sensors was observed due to the offset potentials of the reference electrodes, as described previously in Figure 5, their response slopes and linear regression correlation coefficients are very close. This indicated that the solid-state Ag/AgCl reference electrode showed the comparable performance to the commercial Ag/AgCl reference electrode. It could replace the commercial Ag/AgCl reference electrode, providing possibility for production of the all-solid-state pH sensor.

Table 2 shows the pH values of different buffer solutions and various real solutions obtained from the all-solid-state pH sensor and a commercial glass pH electrode connected to a 510 pH meter (Eutech, US). The all-solid-state pH sensor exhibits a small difference of less than 1 pH unit for all solutions, compared to the commercial glass pH electrode. Large error of pH reading are observed for the highly turbid solutions such as milk and orange juice. Taking values from Table 2, the averaged difference and standard deviation are evaluated to be 0.39 and 0.26 pH unit implying that the all-solid-state pH sensor and the commercial glass pH electrode shows the comparable performance in pH measurement. These deviations probably arise from the absence of the internal liquid electrolyte for the customized all-solid-state pH sensor. However, the all-solid-state pH sensor offers several advantages over the commercial glass pH electrode including low cost, easy fabrication, no fragile component and no internal solution. Since there is no internal solution, the all-solid-state can be miniaturized for the further use in flow injection analysis and microfluidic system.

Table 2: pH values measured from the all-solid-state pH sensor and the commercial glass pH electrode for various liquids

Sample	pH Values Measured from pH Electrode		ΔpH
	All-solid-state	Commercial Glass Electrode	
Buffer pH4	3.82	4.00	0.18
Buffer pH7	6.75	7.00	0.25
Buffer pH10	9.51	10.00	0.49
Coca Cola	2.64	2.75	0.11
Orange juice	2.75	3.53	0.78
Milk	5.98	6.75	0.77
Distilled water	6.97	7.13	0.16
Liquid soap	9.14	9.72	0.58
Liquid detergent	10.96	11.15	0.19

4 Conclusions

In this paper, new solid-state Ag/AgCl electrode has been developed and integrated with the conducting PPy-based pH electrode to fabricate an all-solid-state pH sensor. The solid-state Ag/AgCl has been prepared via electrochemical deposition of Ag on the supporting stainless steel electrode, followed by chlorination to obtain AgCl. XPS and SEM were performed to verify the successful chlorination process showing the partial conversion of Ag to AgCl. Potentiometric response of the solid-state Ag/AgCl electrode was independent upon the pH value of exposed solutions. The all-solid-state pH sensor fabricated by integration of the developed solid-state Ag/AgCl electrode and the polypyrrole-based pH indicative electrode showed a linear potentiometric response of –53.55±1.33 mV.pH^{-1} ($r^2 > 0.99$) over the pH range of 2–12. When tested in various real solutions, the all-solid-state pH sensor showed the comparable performance to the commercial glass pH electrode with small difference in the pH reading. Apart from simple fabrication and low cost, the all-solid-state Ag/AgCl electrode offers an alternative reference electrode without the requirement fragile glass and internal electrolyte. In addition, the developed solid-state Ag/AgCl electrode is possible to be integrated with other solid-state indicative electrodes to create various types of all-solid-state sensors. Our on-going work has been focusing on the miniaturization of the all-solid-state pH sensor for the further use in flow injection analysis and microfluidic system.

Acknowledgments

The authors gratefully acknowledge the Thailand Research Fund (TRF) for the financial support of this research (MRG5380200). A.S. also would like to acknowledge the financial support from the Thailand Research Fund (TRF-RTA) and Royal Thai Government.

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