Stability Enhancement of All-Solid-State H⁺ ISEs with Cross-Linked Silicon-Urethane Matrices

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Abstract
An all-solid-state hydrogen-ion-selective electrode (ASHISE) was fabricated using the polymer hybrid membrane. Polymer membranes composed of Tecoflex polyurethane (TPU), polyvinyl chloride (PVC), silicon rubber (SR), and additives (KTpClPB, DOA, and TDDA) were cast on a carbon rod. The TPU/SR hybrid membrane exhibited a longer lifetime and a higher sensitivity in the sensing of the H⁺ ion compared to conventional TPU/PVC and PVC/SR hybrid membranes. Moreover, the addition of SiCl₄ to TPU-based matrices enhanced the potentiometric response and ISE stability, due to the chemical bonding between Si and C=O in urethane, in which the cross-linking configuration was confirmed by DSC, FT-IR, and XPS experiments. TPU/SR membranes containing SiCl₄ were rendered more stable and showed a pH response over a wide range (i.e., pH 2 – 11.5) with the slope of 60 ± 2 mV/pH for more than four months. The ASHISE exhibited a small interfering potential variation in the wide range of the salt concentration (from 1.0 × 10⁻⁶ M up to 0.1 M). The ASHISE showed a result comparable to a commercial clinical blood analyzer.

Keywords: pH electrode, ISE, All solid state ISE, Polymer membrane, Silicon-urethane matrix

1. Introduction
Hydrogen-ion-selective electrodes (HISEs) play a vital role in various scientific fields. Of these, the liquid-junction type of the glass electrode has been most widely used to date. However, it has some disadvantages such that it should always be stored in a solution while the experiment is not performed, and that it is difficult to fabricate in a small size for miniature applications. Especially, these disadvantages have caused difficulty in the medical industry applications, for example, in the small-volume blood pH analysis and in measurements for implanting purposes [1 – 3]. To overcome these disadvantages, a small and/or flexible HISE needs to be fabricated, which fabrication should avoid the use of an internal solution. Recently, all-solid-state hydrogen-ion-selective electrodes (ASHISEs) using various polymer membranes have been gradually replacing the glass pH electrodes. The reason is that the polymer-membrane-based ASHISE exhibits distinct advantages such as easy miniaturization, mass production, a multi-sensing system, and most importantly, the direct application on substrates.

Many polymer membranes of ASHISEs, such as PVC [4 – 9], room-temperature-vulcanizing (RTV)-type silicon rubber (SR) [10 – 13], and polyurethane (PU) [12 – 14], have been developed and reported. However, PVC-based membranes for ASHISEs require a large quantity of plasticizer due to the high glass transition temperature (Tg) of PVC. In spite of the excellent potentiometric performance of the PVC membrane, it has a limited lifetime [15, 16] due to poor adhesion to the substrate surface and adsorption of biological components on the membrane surface. It is noteworthy here to mention about the SR membrane, because they do not require any additive for self-assembling cross-linking purposes [11 – 14]. Although the pH response of the polymer membrane using SR is good, it shows a non-linear response over a working range [14, 17]. Other membrane materials, such as polyurethane and polyethylene oxide, were cross-linked by exposing the matrices to UV light [18, 19]. The above reports exhibited a good response for pH only in the range of 2 – 10, while the response was not good over pH 10. However, some reports suggest that polyurethane-based membranes for ASHISEs show a good pH response in the range of 2 – 11 [20], and using a Tecoplex polyurethane matrix resulted in a lower protein adsorption and a successful application for the medical field [14]. Earlier studies suggested that the use of SiCl₄ in a polymer membrane having functional groups exhibits a much better potentiometric response and stability of ion-selective electrodes [14, 21, 22].

Thus, we have studied the fabrication of ASHISEs, based on the characteristics of the above mentioned polymers, with polymer membranes which could provide a good response over a wide pH range, a high resistance to interference ions, and a long lifetime. In addition, the present work focused on fabricating a small-size ASHISE which can be applied to the analysis of small volumes of biological fluidic samples. The ASHISE membranes used in this study were composed of polymer matrices of TPU, PVC,
SR, silicon tetrachloride (SiCl$_4$), a hydrogen ion selective ionophore (TDDA), a lipophilic ionic additive (KT$_p$ClPB), and a plasticizer (DOA), in order to achieve flexibility of the polymer matrix and to increase the adhesive property between the polymer membranes and the substrate surface. The experimental parameters affecting the sensitivity and stability of ASHISE, with regard to the contents of the ionophores, the amount of SiCl$_4$, and the ratio of membrane composition, were optimized and examined. Polymer matrices of various compositions were prepared, characterized, and finally applied to the hydrogen-ion sensing after optimizing the experimental conditions.

2. Experimental

2.1. Reagents and Equipment

The reagents and equipments were used as follows: carbon rod (i.d.: 3.0 mm) from Tokai (Tokyo, Japan); graphite powder (< 0.1 mm), potassium tetrakis (p-chlorophenyl) borate (KT$_p$ClPB), dioctyl adipate (DOA: mp = -67 °C, bp = 417 °C), and high-molecular-weight Polyvinylchloride (PVC) from Fluka (Buchs, Switzerland); Tecoflex polyurethane (TPU; SG-80A) from Thermedics (Woburn, MA); room-temperature vulcanizing (RTV)-type silicone rubber (SR: 3140 RTV) from Dow Corning (Midland, MI); tridodecylamine (TDDA) from Eastman Kodak (Rochester, NY); tris-(hydroxymethyl) aminomethane (Tris) from Sigma (St. Louis, MO); tetrahydrofuran (THF), silicon tetrachloride (SiCl$_4$: 1.0 M in dichloromethane), and mineral oil (d.: 0.838) from Aldrich (Milwaukee, WI); and blood/electrolyte control samples from Nova Biomedical (Waltham, MA). Whole blood samples were obtained from a local blood bank (Busan, S. Korea). All other chemicals were of the analytical grade. Aqueous solutions were prepared with doubly distilled water (18.0 MΩ cm).

The potential differences between the working and the reference electrodes were measured using a 16-channel multi pH/Ion meter [Model KST101B, (Kosentech, S. Korea)] with a personal computer. The pHs of the test sample solutions were monitored with a calibrated-glass pH electrode [Model Orion 81-02 ROSS combination pH electrode (Orion, USA)]. Differential scanning calorimetry (DSC) measurements were carried out with a differential scanning calorimeter (Shimadzu, Model TA-50WSi, Japan). X-ray Photoelectron Spectroscopic (XPS) analyses were performed using a VG Scientific Model ESCA Lab 250 XPS spectrometer (KBSI, Busan).

2.2. Fabrication of ASHISEs

As shown in Scheme 1, ASHISE composed of the carbon rod contacted with carbon paste and the polymer layer containing ionophore and additives. A PVC cylindrical holder (i.d.: 3.0 mm; 20 mm length) was used as the body in constructing the ASHISE. Graphite paste was used to electrically connect to the carbon rod (i.d.: 3.0 mm) to the potentiometer, which was made by mixing graphite powder (10 g) with 2 drops of mineral oil, and molded to about 10 mm thickness with the PVC holder. A copper wire (1.0 mm diameter) was inserted through the PVC tube to the graphite paste for the electrical contact. A carbon rod was inserted into graphite paste by means of mechanical pressing and its surface was sequentially polished with 100-, 1000-, and 2000-fine-grade sandpapers, followed by polishing with 0.3 μm alumina to ensure a good clean carbon surface. The upper side of the PVC tube was pretreated with cyanoacrylate resin (Super Pegamento Gel, 3 M) to adhere of the polymer membrane. A 2 μl of a 10 wt% polymer membrane solution was used as a glue to tightly coat the polymer membrane on the carbon rod. After coating the polymer solution onto the carbon surface, the prepared polymer membrane film was immediately cast onto it. In this case, a 500 μl of the 10 wt% polymer membrane solution was used for making the polymer membrane film in the glass ring on a flat Teflon plate.

2.3. Preparation of Polymer Membranes

The membrane cocktails of different compositions given in Table 1 were prepared by dissolving the components in freshly distilled THF. All membranes were prepared by dissolving components of 10 wt% polymer membrane in THF solvent, in the glass rings (i.d.: 2.0 cm). The solvent was allowed to evaporate at room temperature in a dust-free environment for 72 h. Polymer-based membranes were prepared with or without the addition of different amounts of SiCl$_4$ to the membranes.

2.4. Potentiometric Measurements of ASHISEs

Potentiometric responses of ASHISEs were evaluated using a single-junction reference electrode (Ag/AgCl/KCl saturated). Calibration plots were obtained by adding aliquots of LiOH to a background solution of 0.0286 M citric acid/0.0286 M KH$_2$PO$_4$/0.0286 M boric acid/0.0286 M diethyl barbituric acid at room temperature. Dynamic potential
response curves were obtained by the addition of the standard solution to the background electrolyte (0.1 M Tris-HCl, pH 7.0) at room temperature. The solutions were magnetically stirred during the experiment.

3. Results and Discussion

Table 1 presents the polymer matrix composition, dynamic range, and the slope of the pH response observed for the ASHISEs using different polymer membranes, and Figure 1 represents the pH response according to the ratio of polymer membrane composition (in different entry numbers). Membranes 1, 2, and 3 displayed similar responses with slopes of 53.8, 53.9, and 54.0 mV/pH, respectively in the pH range of 2.0 – 9.5. This indicates that the TPU/PVC ratio did not affect the responses and that the linear working range was narrow (pH 2.0 – 9.5). The potential change according to pH was very small above pH 9.5, indicating that these membranes are not suitable for responses above this pH level. To increase the response range and stability of the ASHISEs, we added SiCl4 in polymer membranes.

Membranes 4 – 9 were prepared by adding different amounts of SiCl4 to the composition of membrane 2, and resulting membranes contained 0.17, 0.84, 1.7, 4.1, 7.8, and 14.5 wt% SiCl4, respectively. Slopes of the membranes were 54.0, 56.2, 56.9, 58.4, 60.2, and 63.5 mV/pH, respectively. The slope increased with increasing the concentration of SiCl4, and the linear range for the calibration plots was extended from pH 2 to 10. Membranes 7 and 8, with the addition of 4.1 and 7.8 wt% of SiCl4 showed near-Nernstian slopes (58.4 and 60.2 mV/pH, respectively). To prepare membranes 10,

Table 1. Response properties and compositions of polymer membranes tested in this study (unit: mg). TPU SG-80A: tecoflexpolyurethane; PVC: high-molecular-weight polyvinylchloride; SR 3140RTV: room temperature vulcanizing (RTV)-type silicone rubber; KTpClPB: ionic salt, potassium tetrakis(p-chlorophenyl)borate; TDDA: ionophore, tridodecylamine. DOA: plasticizer, dioctyl adipate; SiCl4: silanizing reagent, silicon tetrachloride.

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<th>SR 3140RTV</th>
<th>KTpClPB</th>
<th>TDDA</th>
<th>DOA [f]</th>
<th>SiCl4</th>
<th>Linear range (pH)</th>
<th>Slope [a] (mV/dec.)</th>
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<td>60.1 ± 1.8</td>
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[a] Data are mean values ± SD for a minimum of four electrodes.
11, and 12, some amounts of SiCl$_4$ were added to membrane 3, resulting in 4.1, 7.8, and 14.5 wt% contents, respectively. In this case, slopes of the membranes were 58.1, 60.2, and 63.5 mV/pH, which were similar to those obtained for the membranes (from 4 to 9) prepared by adding SiCl$_4$ to membrane 2. The same result was obtained for the membrane prepared by adding SiCl$_4$ to membrane 1. The addition of SiCl$_4$ to the TPU/PVC membranes (from 4 to 12) led to the increase of the slope and a slight extension in the linearity of the hydrodynamic range (pH 2 – 10).

In order to obtain a wider pH response range, the membrane 13 was prepared by increasing the amount of ionophore (TDDA), from 4 to 10 wt%, compared with membrane 1. The slope of the pH response increased from 53.8 to 57.1 mV/pH, but the linear range of the calibration plot was the same as that for membrane 1 (pH 2.0 – 9.5). The above results implied that the increase in the amount of SiCl$_4$ would produce a good response due to the increase of the hydrogen-ion transfer. Thus, membranes 14, 15, and 16 were prepared with the additions of 4.1, 7.8, and 14.5 wt% SiCl$_4$, respectively, to membrane 13. Membranes 14 – 16 showed the very wide pH response range, from 2.0 to 11.5, with the slopes of 57.8, 59.7, and 61.7 mV/pH, respectively. The above results indicate that the use of an appropriate amount of SiCl$_4$ and TDDA with TPU/PVC, as in membranes 14, 15, and 16, will render a good response of the ASHISE, specifically a wider pH response range (2.0 – 11.5) with a near-Nernstian slope.

The stability of membranes with and without SiCl$_4$ (membranes 13 and 15, respectively) was tested by storing them in a 50 mM NaHCO$_3$ solution for 20 days. The smooth and transparent surface of the membrane without SiCl$_4$ was changed to the non-transparent state due to swelling after the storage, but the surface of the membrane containing SiCl$_4$ did not exhibit any change after the storage. In addition, the strength of the membranes with and without SiCl$_4$ was examined by a tensile-strength test. The film with SiCl$_4$ was very strong and more elastic. The enhancement of stability by adding SiCl$_4$ to functional-groups-modified PVC- or TPU-based membranes was also reported [14, 23 – 25]. The enhancement of some properties of the membranes caused by the addition of SiCl$_4$ might result from the change in the chemical properties of the membrane by a chemical reaction between SiCl$_4$ and polymer matrices. However, no experimental evidence for a detailed chemical reaction between them has been reported until now.

In order to confirm the chemical reaction between urethane and SiCl$_4$ (mp ~ 70°C, bp ~ 59°C), DSC analyses for membranes 13, 15, and 16 were carried out as shown in Figure 2. Figure 2A shows an endothermic peak at 4°C in a DSC curve recorded for membrane 13 (without SiCl$_4$). By contrast, membrane 15 (Figure 2B), for which 7.8 wt% SiCl$_4$ was added to membrane 13, showed two endothermic peaks, at 4°C and 47°C, respectively. Figure 2C is a DSC curve recorded for membrane 16, which contained 14.5 wt% SiCl$_4$. The Figure also shows two endothermic peaks (a, b) at a similar temperature, and the second endothermic peak (b) is huge compared with that of membrane 15. This indicates that the degree of the bond formation between TPU and Si increased as the amount of SiCl$_4$ increased. These DSC results indicate that the addition of SiCl$_4$ may create the formation of a bond with oxygen (C=O) on the urethane and Si atoms (C–O–Si). In addition, these results revealed an increase in $T_g$ value with increasing concentrations of SiCl$_4$. When the $T_g$ value reached an excessive level, the polymer film become rigid. Hence, the amounts of 2 – 8 wt% SiCl$_4$ were optimum for the purposes of constructing the cross-linked TPU-based membranes.

The FT-IR experiment also confirmed the above results. The spectrum obtained for the TPU-based membranes containing SiCl$_4$ (membranes 15 and 16) showed the absorption band at 1100 cm$^{-1}$ corresponded to the C–O bond, and it was increased as the amount of SiCl$_4$ increased. It might be due to the increased amount of C–O resulting in the formation of the Si–O–C bond [26] at a similar wave number. Moreover, the absorption band at 1640 cm$^{-1}$ obtained for membranes 15 and 16, which contained SiCl$_4$, corresponded to C=N [27]. This absorption band was completely absent in the spectrum for membrane 13 (without SiCl$_4$). The increasing of C–O and C=N band intensity might be due to the cross-linking between C=O in TPU and SiCl$_4$.

Figure 3 shows the XPS spectra of C1s obtained for only TPU and TPU/SiCl$_4$ (= 100/10 wt%) films. Three C1s peaks appeared at about 285, 286.2, and 289.2 eV and corresponded to the C–C, C–O, and N–C=O, respectively, in the case of
only TPU [28]. For TPU/SiCl₄, the peak of the C–C bond appeared at a similar binding energy as found in only TPU, 285.1 eV. Two other peaks of the C–O and N–C=O bonds shifted to the higher binding energies of about 286.5 and 289.6 eV, respectively. These slight shifts in the binding energies of the C–O and N–C=O bonds might be related to the interaction of Si with N–C=O. The height of the C–O peak in the TPU/SiCl₄ film was increased, which might be resulted in the increased C–O bond formation due to the cross-linking between SiCl₄ and the C=O in TPU. Moreover, the decreasing of the N–C=O peak intensity of the TPU/SiCl₄ film supports the cross-linking reaction. Earlier studies showed that SiCl₄ could interact with oxygen and/or nitrogen atoms [29, 30]. In the present study, the interaction between SiCl₄ and the N atom of TPU was difficult in the chemical reaction due to the steric hindrance of the bulky group. Moreover, the O1s spectra for only TPU appeared at 532.5 eV. This peak shifted to the higher binding energy of 532.9 eV for TPU/SiCl₄, indicating the interaction of SiCl₄ with the oxygen atom. Based on the DSC, FT-IR, and XPS results, a schematic representation of the cross-linking that occurred between the C=O site in TPU and SiCl₄ is shown in Figure 4.

The lifetime of the ISE fabricated with membrane 15 was evaluated by monitoring the change of the response over four months, as shown in Figure 5. Up to 40 days, a slight decrease in the slope from its initial value was found. After 40 days, the slope decreased by about 50%. To obtain a more stable ISE, the polymer membrane was modified with SR. Membrane 17 was prepared by adding 1.7 wt% SR to membrane 3 and was investigated for the pH response. This membrane exhibited a slope of 52.5 mV/pH, which is 1.5 mV lower than that of membrane 3. However, membrane 17 exhibited a wider response range (pH 2.0–10.5) than that of membrane 3 (pH 2.0–9.5). To attain a wide pH response range, the membrane composition was changed to that of membrane 18 (PVC/SR). Membrane 18 exhibited a wide response range (pH 2.0–11.5) with a slope of 52.8 mV/pH. Up to 60 days, this membrane displayed a similar potential response with a slope of 52.0±2.0 mV/pH. After 60 days, a decrease in the response of the ISE was observed (Figure 5). As mentioned above, the slope was lower than a Nernstian slope and the lifetime of the ASHISE was short using membrane 18.

In order to attain a long lifetime and a wide response range with a better Nernstian slope in the pH, the membrane composition was replaced by TPU/SR (membrane 19). Membrane 19 exhibited a wider pH response range (pH 2.0–11.5) with the slope of 58.2 mV/pH. As discussed

Fig. 3. X-ray photoelectron spectra for TPU with and without SiCl₄.

Fig. 4. Schematic diagram for cross-linkage of TPU-based polymer matrices with silanizing agent (SiCl₄).
above, the TPU-based membranes containing SiCl\textsubscript{4} showed a good response and stability. Hence, by adding SiCl\textsubscript{4} to membrane 19, membranes 20–22 (1.6, 4.1, and 7.8 wt% SiCl\textsubscript{4}, respectively) were prepared. In these cases, all the membranes showed a wide pH response range with a Nernstian slope. The increased amount of SiCl\textsubscript{4} in the TPU/SR membranes led to the increase of the slope from 59.2, 60.1 to 63.2 mV/pH, respectively. This might be due to the higher response resulting from the presence of ionic sites (an ionizable silicon network) within the TPU/SR membranes containing SiCl\textsubscript{4}. Membranes 20 and 21 each exhibited super Nernstian slopes. Lifetimes for these membranes were examined and the result, for membrane 21 only, is presented in Figure 5. These membranes showed good responses with slopes of 58.5 ± 0.2 mV/pH over four months.

The ASHISE prepared using membrane 21 was examined for the interference effect caused by several other cations and anions at high concentrations up to 0.1 M, which were added to the 0.1 M Tris-HCl buffer solution (pH 7.0). The dynamic potential response was compared with that of a conventional liquid-junction type of the glass pH electrode (Orion, USA). As shown in Figure 6, a similar potential drift was observed for the ASHISE and of the conventional glass electrode, caused by the interference effect of various salts (LiCl, KCl, CaCl\textsubscript{2}, KNO\textsubscript{3}, MgCl\textsubscript{2}, NaCl, Na-salicylate, and NaHCO\textsubscript{3}).

To examine the performance of ASHISE fabricated using membrane 21 for a real sample, the blood-pH analysis was carried out with a home-made shut-tight-type flow cell in order to protect coagulation of blood due to the direct contact of air. In this experiment, the ASHISE and the reference electrode (Ag/AgCl) were installed into the flow cell, respectively. The pH sensing device was calibrated employed a two-point (pH 7.0, and 8.0) method and then determined pHs of human blood samples. The results were compared with one obtained from a commercially available clinical blood analyzer (Nova System, USA). We obtained an excellent agreement between the results employing ASHISE and the commercial blood analyzer as shown in Table 2.

4. Conclusions

The ASHISE fabricated in the present study exhibits many advantages when compared with previous studies. The
advantages include the addition of SiCl₄ to TPU-based membranes which enhance lifetime and potentiometric response due to the cross-linking between Si and C=O in TPU. In this case, using 2–8 wt% SiCl₄ was enough to construct the cross-linked TPU-based membranes. The cross-linking formation was confirmed from the results of DSC, FT-IR, and XPS experiments. Among the polymer matrices, TPU/SR-based membranes showed the best sensitivity and the widest pH response range (2.0–11.5) with a good Nernstian slope (60.0 mV/pH). In addition, these membranes showed good responses and stable slopes of 58.5 mV/C₆O₂ at high concentrations (up to 0.1 M) and gave similar results to those of a conventional glass pH electrode. Moreover, the ASHISE fabricated with membrane 21 was studied in the presence of other ions at high concentrations (up to 0.1 M) and gave similar results to those of a conventional glass pH electrode. Moreover, the ASHISE showed the possibility of fabricating a miniaturized sensor easily and with less cost using it in medical instruments which demand a long lifetime and stability.

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6. References