Disposable Solid-State pH Sensor
Using Nanoporous Platinum and Copolyelectrolytic Junction[†]

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A disposable solid-state pH sensor was realized by utilizing two nanoporous Pt (npPt) electrodes and a copoly-electrolytic junction. One nanoporous Pt electrode was to measure the pH as an indicating electrode (pH-IE) and the other assembled with copolyelectrolytic junction was to maintain constant open circuit potential (E_{oc}) as a solid-state reference electrode (SSRE). The copolyelectrolytic junction was composed of cationic and anionic polymers immobilized by photo-polymerization of *N,N'*-methylenebisacrylamide, making buffered electrolytic environment on the SSRE. It was expected to make. The nanoporous Pt surrounded by a constant pH excellently worked as a solid state reference electrode so as to stabilize the system within 30 s and retain the electrochemical environment regardless of unknown sample solutions. Combination between the SSRE and the pH-IE commonly based on nanoporous Pt yielded a complete solid-state pH sensor that requires no internal filling solution. The solid state pH sensing chip is simple and easy to fabricate so that it could be practically used for disposable purposes. Moreover, the solid-state pH sensor successfully functions in calibration-free mode in a variety of buffers and surfactant samples.

Key Words: Nanoporous platinum, Copolyelectrolyte junction, Solid-state pH sensor, Disposable pH sensor, Calibration-free pH sensor

Introduction

A pH measuring device has been essentially required for various purposes, and a few types of pH sensors have been developed to meet such demands. However, most of the pH sensors, which are currently available and being used in practice, are glass membrane combination electrodes. They are fragile, expensive and bulky so as to be handled with care, always kept in the storage solution when not used, and mandatorily calibrated before use.

Solid-state pH sensor has been one of the potential alternatives to overcome these drawbacks of glass membrane combination electrodes.[1-10] For example, the hydrogen ion sensitive field-effect transistors (H^{+}-ISFET),[1] metal oxides (iridium oxide,[2-4] platinum oxide[5]), and H^{+}-selective electrodes based on poly (vinylchloride)/polyurethane membrane containing tridodecyl-amine[6,7] were proposed as new pH-indicating electrodes (pH-IEs). These solid state pH-IEs exhibited good performance, but they still use reference electrodes (REs) such as Ag/AgCl/KCl(*aq*) with filling solution and liquid junction that hamper miniaturization and mass-production of the whole pH sensor system. For the disposable purpose of point-of-care test (POCT), the pH sensors are often prepared on a chip, which could be fully miniaturized and friendly to mass-production. For this reason, the solid-state reference electrode (SSRE) without filling solution or liquid junction has been studied to be integrated in

a microchip.[6,7] Many attempts have been made to develop successful SSRE by covering Ag/AgCl with electrolyte-doped polymer,[8,9] poly(vinylchloride) membranes with plasticizer, lipophilic salt, or cation or anion exchanger,[10] KCl containing hydrogel layer,[6] polyurethane,[7] or electrolyte loaded polymers.[11,12] However, the present SSREs are not sufficiently reproducible and need long stabilization period.

Reportedly, nanoporous Pt (npPt) electrode shows far better pH sensing performance than flat Pt electrode[5] by virtue of low polarizability resulting from extremely enlarged electrode surface area. In addition, npPt can act as a good RE when it is in buffer solutions.[13]

In this contribution, a new type of SSRE is proposed by covering npPt with polyelectrolytes which maintain a constant pH like a pseudo buffer. The polyelectrolyte mixture consisting of weak acidic or basic functional groups such as poly(acrylic acid) (PAA), poly(ethyleneimine) (PEI), and their copolyelectrolyte (PEI-*co*-PAA) were suggested and tested. Harnessing the proposed SSRE, a solid-state pH sensor was successfully prepared on an alumina substrate.

Experimental

Reagents. Sodium tetraborate, boric acid, citric acid, sodium citrate, *tert*-octylphenoxypolyethoxyethanol (Triton X-100), hydrogen hexachloroplatinate hydrate (HCPA), polyacrylic acid (PAA, #323667, average Mw ~1800), polyethyleneimine (PEI, #482595, average Mw ~1300, 50 wt % in water), 2-hydroxy-4'-(2-hydroxyethoxy)-2-methylpropiophenone (photo-

initiator), N,N'-methylenebisacrylamide (cross linker), and dimethylsulphoxide (DMSO) were purchased from Sigma. NaH_2PO_4 (98%), Na_2HPO_4 (98%), and KCl (99.5%) were purchased from Junsei Chemical.
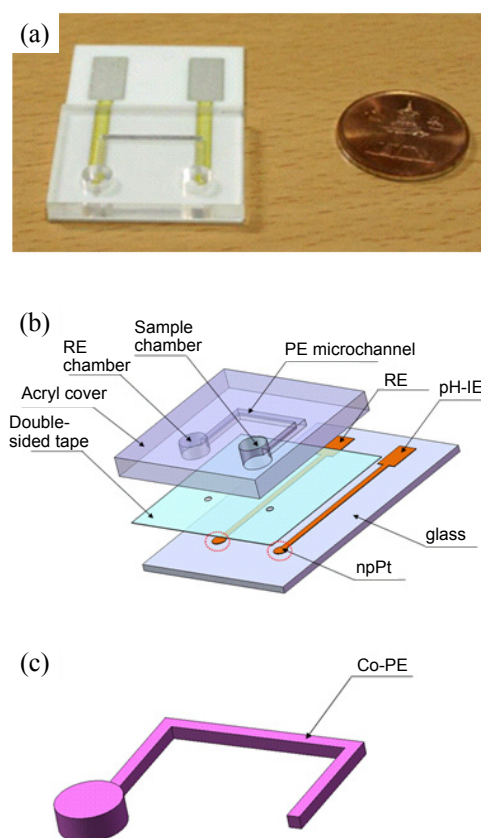
Fabrication of solid-state RE and pH sensor. Au conducting patterns were prepared on alumina substrate by subsequent screen-printing of Au paste and dielectric silica (as insulating coating) followed by thermal curing at 800 °C. The npPt was electroplated on the Au conducting pattern and the real surface area of npPt was measured where a conversion factor was 210 $\mu C\ cm^{-2}$, following the same method reported previously.[5,14] The electroplated npPt was coated with polyphenol membrane and used as pH-IE.[5] The channel and chambers were fabricated by a conventional computer numerical control machine (Hwacheon Inc., Korea). The polyacrylate plate, briefly called acryl cover, was dipped in trimethylailylmethylamine, TMSMA, solution (Sigma) and kept in a vacuum chamber for 30 min. An alumina substrate with npPt and a cover plate with a microchannel and chambers were bonded to each other with silicone double-sided adhesive tape (Youngwoo, Korea) by applying thermal pressure (Seoul system, Korea).

The polyelectrolytic (PE) junction in this study is a polymeric salt bridge in which a constant pH and high ionic conductivity are maintained. Two polymers with weak base and acid functional groups were employed for this 'PE junction', PEI and PAA. The proposed PE junction was fabricated according to previously reported method with some modification.[15] A solution containing PEI or PAA (50 wt %) and photo-initiator (2 wt %) was prepared using DI water (solution **A**). To prepare PEI-*co*-PAA junction, both PEI and PAA were used in 1:1 (wt) ratio. The other solution containing cross linker (5 wt %) was prepared using 1:1 (vol) solvent mixture of DMSO and DI water (solution **B**). A solution for photo-polymerization was prepared by mixing solution A and B in 3:1 (vol) ratio. The photo-polymerization was performed by aligning a mask to let only the PE microchannel and RE chamber exposed, and then by illuminating UV light (365 nm, 16 mW cm⁻², 60 s). After photo-polymerization, the residual solution was removed and rinsed twice with 1 M KCl and DI water.

Results and Discussion

Figure 1 illustrates the structure of the solid-state pH sensor proposed in this study. There are a pH-IE and a RE on an alumina substrate, between which a PE junction in the PE microchannel are present. The whole chip was constructed by assembling of the alumina substrate and the mechanically machined cover plate. npPts were electroplated on the two identical circular areas (2 mm in diameter) of the Au conducting patterns to be used as a pH-IE and a RE. The npPt for pH-IE was exposed to sample solution in the sampling chamber (4 mm in diameter). The other npPt was assembled with PE junction and used as a SSRE.

The role of the PE junction can be explained by imagining a polyelectrolyte plug between a pair of electrodes. The schematics in Figure 2 show three cases of PE junctions made of cationic PEI ($pK_a = 5.5$), anionic PAA ($pK_a = 4.3$) or mixed PEI-*co*-PAA layer. When PEI or PAA fills in the RE chamber and the PE
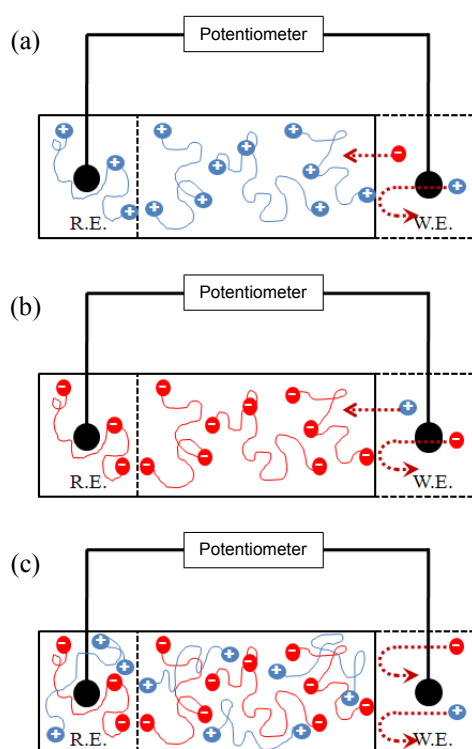

Figure 1. (a) Photogragh of the proposed solid-state pH sensor. (b) Schematic diagrams of the solid-state pH sensor and (c) the RE chamber and PE microchannel filled with the polyelectrolytic mixture, 'PE junction'.

microchannel, the pH in the PE junction is determined by the acid-base equilibrium of the polymeric functional groups. If PEI or PAA is filled in the microchannel and RE chamber, the PE plug allows only flow of counter ions due to electrostatic repulsion. The counter ions from the unknown sample solution may modify the conductivity of the PE junction and even contaminate the RE surface. Such an effect appears as time passes after the system is exposed to the sample solution. As a consequence, the pH near the npPt of RE may be affected by the sample solution as shown Figure 2(a) and 2(b). In addition, it should be noted that the pH in the RE chamber is maintained around pK_a of the polymeric functional groups. So the buffer capacity may be insufficient at a pH which is far from the polymeric pK_a.

These problems are expected to be alleviated by mixing two acidic and basic polymers. The mixed PEI-*co*-PAA has both cationic and anionic sites as stationary phase, which needs only a limited amount of mobile ions to maintain the potentiometric circuit. Minimizing the ion transport through PEI-*co*-PAA junction and retaining sufficient ionic conductivity, the potential drop across PE is negligible.[16,17] Furthermore, the two separate pK_as of the polymer mixture widen the pH gamut where the buffer capacity is enough.

Open circuit potential (E_{oc}) of the SSRE was checked *versus* a conventional liquid junction Ag/AgCl RE (BAS model RE-5B) in 0.1 M PBS of pH 2, 7, 12 (Figure 3). The E_{oc} of the npPt
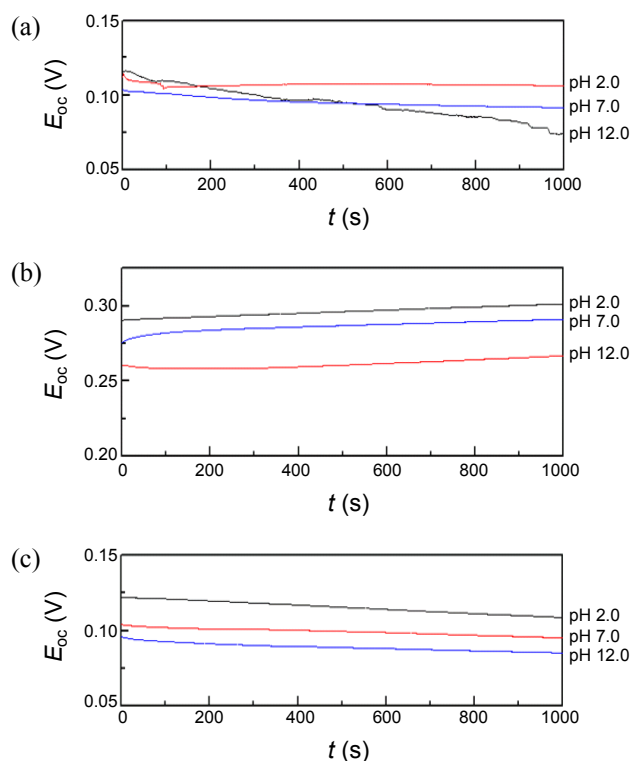
Figure 2. The working principle of PE junction in maintaining constant pH environment; (a) cationic PE (PEI), (b) anionic PE (PAA), and (c) mixed PE of opposite charge (PEI-*co*-PAA).

Figure 3. E_{oc} of SSRE with (a) PEI, (b) PAA, and (c) PEI-*co*-PAA in 0.1 M PBS (pH 2.0, 7.0, 12.0) as a function of time exposed to sample solutions.

Figure 4. E_{oc} of SSRE *versus* Ag/AgCl in (a) 0.1 M PBS of various pH (2, 4, 6, 8, 10, and 12) and (b) PBS solution of various ionic strength (from 0.1 M to 0.1 μM).
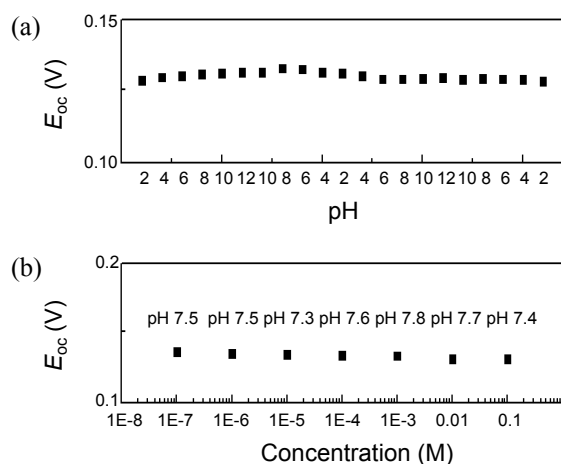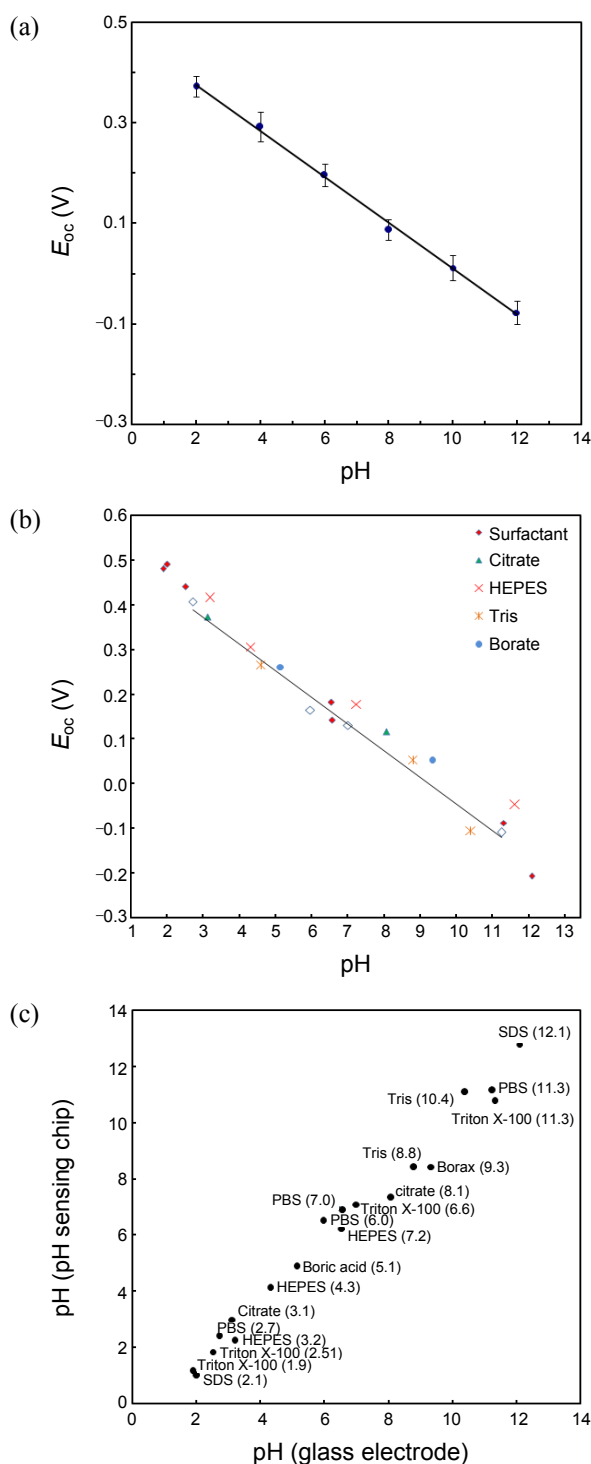
assembled with PEI (npPt/PEI) drifted continuously, as shown Figure 3(a). As for npPt/PAA, E_{oc} was stable compared with that of PEI (Figure 3(b)). E_{oc} of npPt/PEI-*co*-PAA was quickly stabilized to a constant value that was maintained at least for 1000 s. On the whole, the E_{oc} of npPt/PEI was more negative than those of the npPt assembled with PAA (npPt/PAA). That is not surprising by noting that the pK_a of PEI is higher than that of PAA. The effect of the pH of sample solution was small but not ignorable in the case of the E_{oc} of npPt/PEI and npPt/ PAA. In comparison with the E_{oc}s of npPt/PEI and npPt/PAA, E_{oc} of the npPt assembled with PEI-*co*-PAA (npPt/PEI-*co*-PAA) showed relatively lower variation responding to pH and needed shorter period for stabilization. These phenomena can be largely understood on the basis of selective ion mass transport through the PE junction and the pH range where effective buffering is valid.

Based on the results of less drifts and lower sensitivity to the pH change of the sample solution, PEI-*co*-PAA was chosen as a material for the PE junction of SSRE. Figure 4(a) shows that the E_{oc} of npPt/PEI-*co*-PAA was independent of pH variation between 2 and 12 and the standard deviation of the E_{oc} was about 5 mV. Moreover, the E_{oc} of npPt/PEI-*co*-PAA negligibly depended on the ionic strength of the sample solution and was constant in a wide range of ion concentration (0.1 M ~ 0.1 μM).

Figure 5(a) shows the pH responses of the combined system consisting of the npPt with a polyphenol membrane (npPt/PPh) as a pH-IE and npPt/PEI-*co*-PAA as a SSRE. The E_{oc} of the pH sensing chip exhibited reproducible and linear responses in

the pH range between 2 and 12. In the previous report,[5] polyphenol membrane on the npPt suppressed the interference and enhanced the performance of npPt as a pH-IE. The slope of −45.0 mV per pH of the npPt/PPh was similar to that reported previously.[5] pH measurements were carried out with the proposed chip, in which a npPt/PPh (pH-IE) and a npPt/PEI-*co*-PAA (SSRE) were integrated, for a variety of practical samples, including buffers (PBS, citrate, borate, TRIS, HEPES) and surfactant (SDS, Triton X-100) (Figure 5(b)). The responses were

(a)

(b)

(c)

Figure 5. E_{oc} responses of npPt/PPh *versus* npPt/PEI-*co*-PAA in (a) 0.1 M PBS (pH 2, 4, 6, 8, 10, 12) ($n = 5$, slope: −45.0 mV, correlation factor: 0.998) and (b) a variety of buffers (PBS, citrate, HEPES, Tris, borate) and surfactants (SDS, Triton X-100). The pH values were measured by a commercial pH glass electrode (Orion, USA). (c) Correlation between pH values measured with a solid-state pH sensor and with a calibrated pH glass electrode.

linear and accurate with a limited deviation from the trend line. Good accuracy and linearity of the present pH sensor suggest the possibility of calibration-free pH sensing by constructing a

general conversion correlation between E_{oc} and pH and then by converting the measured E_{oc} to pH. The E_{oc} responses presented in Figure 5(b) shows a conversion correlation of $E_{oc} = -59$ pH + 549. Using this common conversion equation, the acquired E_{oc} data in Figure 5(b) were converted into pH values and checked out how they were consistent with the true values. Figure 5(c) shows the correlation between the pH values converted from the E_{oc} of the proposed solid state pH sensing chip and measured by calibrated pH glass combination electrode. The results tell that calibration-free pH sensing using this solid state chip system is promising.

Conclusion

A disposable solid-state pH sensor composed of two nanoporous Pt (npPt) electrodes and a copolyelectrolytic (PEI-*co*-PAA) junction was proposed and evaluated. The npPt with a polyphenol membrane (npPt/PPh) and npPt/PEI-*co*-PAA were employed as a pH-IE and a SSRE, respectively. The SSRE based on PEI-*co*-PAA was quickly stabilized within 30 s and rarely affected by the chemical environments of sample solution at least for 1000 s. These results are good enough for disposable applications. Harnessing the reliable performance of the SSRE, the proposed solid state pH sensor showed the capability of successful calibration-free pH sensing. The solid-state pH sensing chip in this study is mass-production friendly, easy to be miniaturized, cost effective owing to the absence of internal solution or liquid junction. Moreover, the alumina substrate and the transparent plastic cover plate are practical and cost effective alternatives to silicon substrate or glass. Consequently, this disposable and calibration-free solid state pH sensor is expected to make significant contributions to the biochemical, medical and analytical applications.

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