

우수한 전기화학적 센싱 성능을 지닌 티타늄 와이어 기반의 휴대 및 일회용 pH 센서 개발

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Development of a Portable and Disposable pH Sensor Based on Titanium Wire with High Electrochemical Sensing Performance

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초 록

본 연구에서는 하이드로늄 이온 농도를 모니터링하기 위한 티타늄(Ti) 와이어를 기반으로 하는 휴대용 일회용 pH 센서를 성공적으로 개발하였다. 센싱 전극은 Ti 와이어에 이리듐 산화물을 전기화학적으로 증착하여 제조하였고, 기준 전극으로 Ti 와이어에 Ag/AgCl 잉크를 코팅하였다. pH 센서에 두 개의 전극을 결합한 후 pH 센서를 다양한 pH 용액에 담그면 개방 회로 전위 신호를 수집할 수 있다. 상기 제조된 pH 센서는 감도, 응답 시간, 반복성, 선택도 및 안정성 측면에서 우수한 전기화학적 감지 성능을 보여 주었다. 현장 검사 응용을 시연하기 위해서 pH 센서를 모바일 애플리케이션과 통신할 수 있는 무선 전자 모듈과 통합하였다. 이 휴대용 pH 센서는 실제 샘플의 pH 변화를 정확하게 측정했으며 결과는 상용 pH 측정기의 데이터와 일치하였다.

Abstract

A portable and disposable pH sensor based on Ti wire was successfully developed for monitoring hydronium ion concentrations. A sensing electrode was prepared by electrochemically depositing iridium oxide onto a Ti wire, while a reference electrode was fabricated by coating Ag/AgCl ink on a Ti wire. Combining the two electrodes in the pH sensor enabled the collection of open circuit potential signals when the sensor was immersed in solutions of various pH values. The pH sensor exhibited excellent electrochemical sensing performance in terms of sensitivity, response time, repeatability, selectivity, and stability. To demonstrate point-of-measurement applications, the pH sensor was integrated with a wireless electronic module that could communicate with a mobile application. The portable pH sensor accurately measured pH changes in real samples. The results obtained were consistent with those of using a commercial pH meter.

Keywords: pH sensor, Electrochemistry, Titanium, Electromotive force, Iridium oxide

1. Introduction

Over decades, the analysis of hydronium ion concentration in solutions has been a significant requirement in various applications in agriculture, environmental monitoring, food manufacturing, wastewater treatment, industrial processes, and research development[1-6]. Furthermore, pH monitoring is employed to determine the health status of people[7-10]. Solutions that contain a dominant concentration of H⁺

ions are highly acidic, while those that contain more OH⁻ ions are highly basic. Commercially available pH meters based on electrochemistry comprise a sensor electrode and reference electrode, which are made up of porous and permeable glass bulbs. The pH value, that is, the hydronium ion concentration, corresponds to the Nernst equation as follows.

$$E = E^{\circ} - 0.0591 \text{ pH}$$

where E and E^o represent the cell potential and standard cell potential, respectively. Although glass-type pH meters exhibit high sensitivity, repeatability, and long-term stability in several applications, the brittleness and size of the glass-type meter and solution-supported elec-

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trodes limit the area and volume of the samples. Consequently, glass-type pH meters are unsuitable for certain applications, such as microscale environments, in vivo biomedical monitoring, and strong acidic and alkaline solutions.

To date, various mechanically strong and miniaturized pH sensors have been developed[9,11]. Compared with conventional solution-supported electrodes, solid-state electrodes have also been developed for fabricating pH sensors. Metal oxides (e.g., RuO₂, MnO₂, TiO₂, IrO_x, and PtO₂) and conducting polymers (e.g., polyaniline and polypyrrole) have been widely explored as sensing electrode materials[12-18]. In particular, the synthesis of iridium oxide films on metal substrates for pH sensors facilitates super-Nernst behavior, stable potential, fast response time, and chemical stability[19-22]. Iridium oxides can be synthesized using sputtering deposition, thermal oxidation, electroplating deposition, and electrochemical deposition methods[15, 19,21-23]. These methods enable the fabrication of various types of pH sensors, such as films, wires, needles, meshes, and foams[21-26].

In this study, we developed a portable and disposable pH sensor based on a Ti wire prepared by electrochemically depositing iridium oxide. A reference electrode was prepared by coating Ag ink on a Ti wire, followed by electrodepositing Cl ions. The resulting pH sensor wire exhibited Nernstian sensitivity, fast response time, repeatability, and potential stability. Further, practical applications were demonstrated by integrating a pH sensor wire with a wireless electronic module capable of communicating with a mobile application. Real samples of tap water, wastewater, and seawater were tested using a pH sensor wire, demonstrating accurate and quantitative pH measurements.

2. Experimental

2.1. Reagents and materials

In this study, aniline (99.5%), sulfuric acid, hydrogen chloride, sodium hydroxide, potassium hydrogen phthalate, potassium dihydrogen phosphate, tris(hydroxymethyl)aminomethane, borax, potassium chloride, calcium chloride, magnesium chloride, ammonium chloride, and titanium wire were obtained from Sigma-Aldrich.

2.2. Fabrication of pH sensor

The pH sensor wires were fabricated using the electrochemical deposition method using Ti wires. As the sensing electrode, polyaniline materials were electrochemically deposited on the Ti wire using cyclic voltammetry (CV) over 100 cycles in the potential range of -0.1 to +0.8 V under a 3-electrode system. The electrolyte used was a 0.5 M aniline monomer that was dissolved in 1 M H₂SO₄. The reference electrode was prepared by coating Ag/AgCl on a Ti wire. The Ag/AgCl-Ti wire was coated with Cl-containing polyvinyl butyral (PVB) to ensure the potential stability of the sensor. A printed circuit board (PCB) was made by customized system in our group according to the previously reported result[9].

2.3. Characterization

Scanning electron microscopy (SEM) images were obtained using a

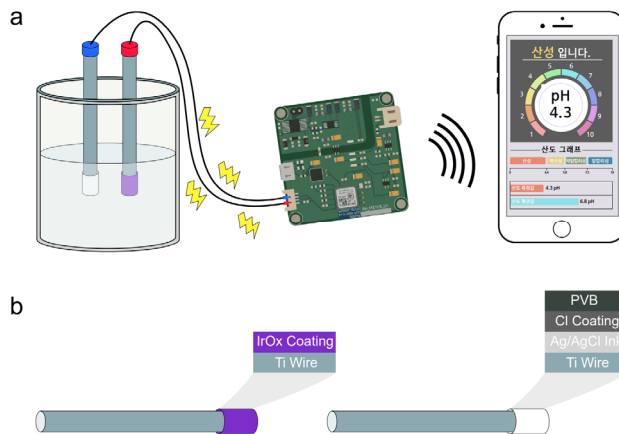


Figure 1. Schematic of the (a) concept of our portable and disposable pH sensor system and (b) cross-sectional structure of the sensing and reference electrodes.

field-emission scanning electron microscope (JSM-6701F, JEOL Ltd.). Optical microscopy (OM) images were obtained using an optical microscope (BX53MTRF-S, OLYMPUS). Electrochemical characterization was performed using a CHI 760E instrument (CH Instruments, Inc.). To measure electromotive force (EMF) signals, solutions with different pH values of 2.0–10.0 were used. The electrochemical sensing performance of the pH sensor was evaluated using a potentiometric technique.

3. Results and Discussion

The concept of the portable and disposable pH sensor system is illustrated in Figure 1(a). The pH sensor wire comprised two electrodes, IrOx- and Ag/AgCl-coated Ti wires, for the sensing and reference electrodes, respectively[Figure 1(b)]. In addition, Cl-containing PVB was coated onto the surface of Ag/AgCl to ensure the potential stability of the reference electrode. The as-prepared pH sensor wire was connected to an electronic module. The overall system of the electronic module comprised interface circuits, a microcontroller, an analog-to-digital converter, Bluetooth low energy, and a lithium-ion battery (3.7 V). This electronic module enabled the collection of data from the sensor, which were transferred to a user's mobile application. The user can easily access the mobile application using a smartphone; the application processes the sensor signals and displays a value or graph for the users.

The sensing and reference electrodes were fabricated using the electrochemical deposition method. The CV technique facilitated the uniform and conformal coating of IrOx[Figure 2(a)]. The OM and SEM images revealed that the IrOx nanoparticles were uniformly distributed on the Ti surface. The reference electrode was prepared by coating Ag/AgCl ink and PVB on the surface of the Ti wire. In particular, the Cl ions were electrochemically deposited on the Ag/AgCl surface for potential stability[Figure 2(b)]. As shown in the OM and SEM images [Figure 2(b)], Ag/AgCl and PVB were uniformly coated onto the Ti wire.

The electrochemical performance of the pH sensor was evaluated by measuring the EMF of the sensor immersed in different buffer sol-

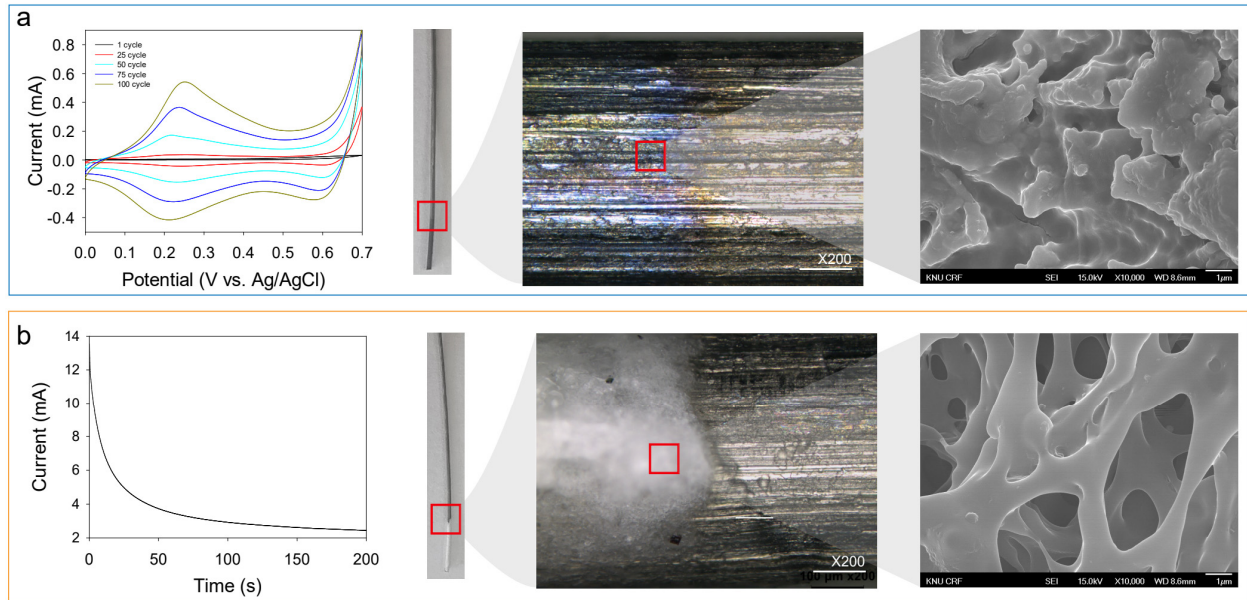


Figure 2. Electrochemical deposition results and digital, OM, and SEM images of the (a) sensing and (b) reference electrodes.

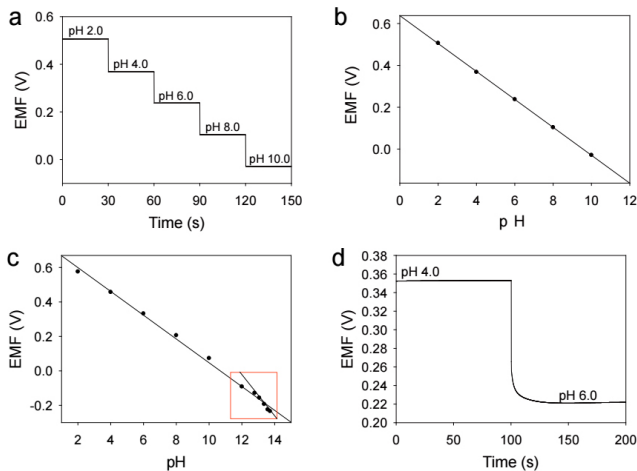


Figure 3. (a) EMF responses of the pH sensor for pH values increasing from 2.0 to 10.0. (b) Calibration curve of the pH sensor. (c) Limit of detection of the pH sensor. (d) Response time result for the pH sensor.

utions using the potentiometric technique. Figure 3(a) shows the typical EMF responses of the pH sensor. The EMF signal decreased as the pH increased. The pH sensor showed a linear calibration curve based on the EMF versus pH plot. The slope was calculated to be 66.7 mV/pH ($R^2 = 0.9999$) over a wide pH range of 2.0–10.0, which is consistent with the Nernst equation [Figure 3(b)]. The limit of detection was calculated to be pH 12.78 [Figure 3(c)]. The pH sensor exhibited a fast response time of 4.0 s [Figure 3(d)]. To demonstrate reproducibility, the sensitivities of five sensors were tested. The sensors exhibited an average sensitivity of 66.7 mV/pH with a small standard deviation of 0.50, indicating the good reproducibility of electrochemistry based fabrication for pH sensors [Figure 4(a)]. Figure 4(b) shows the repeatability

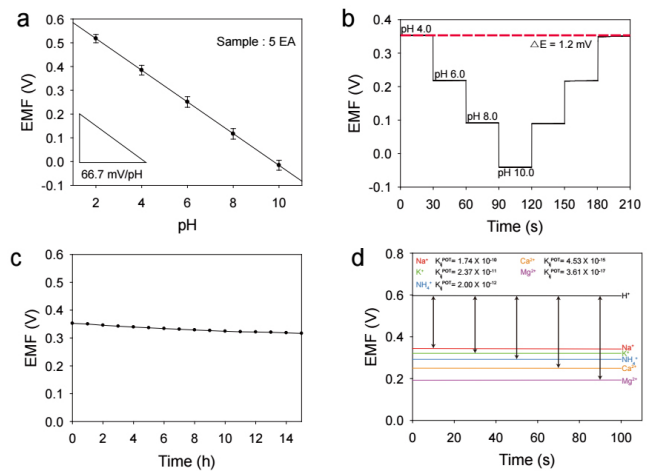


Figure 4. (a) Calibration curve of EMF versus pH for the pH sensors ($N = 5$). (b) Repeatability of the pH sensor recycling measurement for solutions of different pH. (c) Potential stability test of the pH sensor measured in pH 8 for 15 h. (d) EMF responses of pH sensor immersed in various interfering ion solutions, such as Na^+ , Ca^{2+} , Mg^{2+} , K^+ , and NH_4^+ 10 mM.

test of the pH sensor, which was performed by measuring the EMF responses of the pH sensor under a titrated cycle at pH values of 4.0, 6.0, 8.0, and 10.0. The sensitivities of the pH sensor were 65.8 and 66.1 mV/pH for the forward and backward directions, respectively. The small variation between the two sensitivities indicates the excellent reusability of the pH sensor. The potential stability of the pH sensor was further investigated by measuring the EMF responses of the pH sensor immersed in pH 8 over 15 h [Figure 4(c)]. The EMF signals remained almost constant, resulting in a potential drift of 2.4 mV/h. This corresponds to an error of 3.5% per hour for the pH sensitivity.

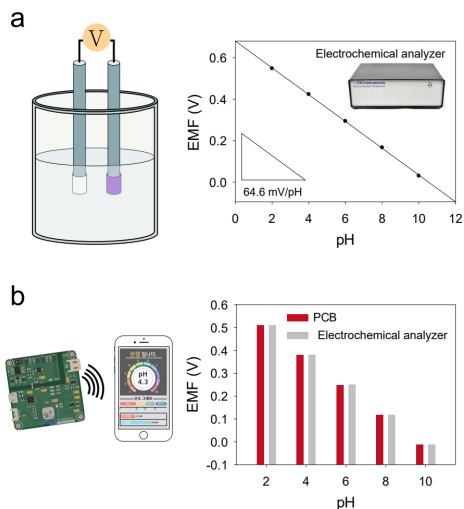


Figure 5. (a) pH calibration curves of the pH sensor obtained from an electrochemical analyzer. (b) EMF responses of the pH sensor obtained from the PCB module and electrochemical analyzer for solutions of different pH.

This result indicates the excellent long-term stability of the pH sensor. As the real sample solutions have various electrolyte ions, the pH sensor should selectively detect and measure the hydronium ions in the presence of other ions. The selectivity of the pH sensor was investigated using the IUPAC recommended separate solution method. Ca^{2+} , K^+ , Na^+ , Mg^{2+} , and NH_4^+ were tested as interfering ions. The EMF signals of the pH sensor were measured in a mixture containing different cations at the same concentration of 10 mM. The EMF signals and selectivity coefficient values of the pH sensor against the interfering ions are shown in Figure 4(d). All values for the pH sensor are below 10^{-10} . Based on the IUPAC recommendation that a K value < 1 indicates good selectivity, the pH sensor can accurately quantify the concentration of hydronium ions in the presence of interfering ions[27-30].

A portable and disposable pH sensor was realized by devising a pH sensor system integrated with a PCB. A custom-designed mobile application displayed the measured pH value. To ensure the performance of the PCB, we compared the sensitivity of the pH sensor with those of the PCB and electrochemical analyzer (CHI 760D instrument, Figure 5(a)). The sensitivity of 65.2 mV/pH obtained from PCB was similar to that of the electrochemical analyzer[64.6 mV/pH, Figure 5(b)]. This result indicates that the PCB-integrated pH sensor can accurately measure the hydronium ion concentration in the solution. The wire-type pH sensor allowed us to measure the pH in a limited volume and area of the sample. The pH sensor exhibited a sensitivity of 65.0 mV/pH across a wide pH range of 2.0–10.0 with a sample volume of 30 mL, which was consistent with that obtained using a sample volume of 3 mL.

The portable pH sensor was tested using real samples of tap water, seawater, agricultural wastewater, and domestic wastewater[Figure (6)]. A commercially available pH meter (METTLER TOLEDO Seven-Compact™ S220) was also used to determine the pH values. The pH sensor quantified the pH values of the real samples accurately as 8.3,

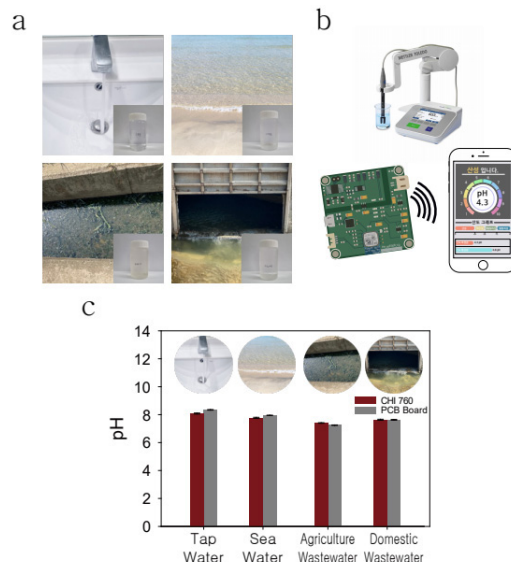


Figure 6. (a) Digital images of tap water, seawater, agriculture wastewater, and domestic wastewater. (b) Illustration of the pH sensor and pH meter. (c) pH values determined by the pH sensor, obtained from the PCB module and electrochemical analyzer with real samples.

7.9, 7.3, and 7.6 for the tap water, seawater, agricultural wastewater, and domestic wastewater, respectively. These pH values were similar to those obtained using a commercial pH meter. Compared to the pH meter, the pH sensor is more efficient in terms of point-of-measurement, simple operation, and easy management. In addition, because the Ti wire-based electrodes are disposable, sensor damage from real samples, which is a critical issue for glass-type electrodes, can be avoided.

4. Conclusion

A portable and disposable pH sensor, based on a Ti wire for the point-of-measurement of hydronium ion concentration in several applications, was fabricated. A sensing electrode was prepared by electrochemically depositing iridium oxide onto a Ti wire, and a reference electrode was created by coating Ag/AgCl ink on a Ti wire. The as-prepared pH sensor exhibited a high sensitivity (66.7 mV/pH), fast response time (4.0 s), good repeatability, good selectivity, and excellent long-term stability. A portable and disposable pH sensor system was developed by combining it with an electronic module. The electrochemical performance of the pH sensor obtained from the electronic module was consistent with that of the pH sensor obtained from an electrochemical analyzer. Various real samples of tap water, seawater, agricultural wastewater, and domestic wastewater were tested using the pH sensor, demonstrating its reliable and reproducible performance.

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