

pH-Sensitive Solid-State Electrode Based on Electrodeposited Nanoporous Platinum

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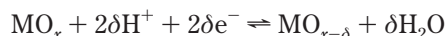
The nanoporous platinum oxide (H₁-ePtO) as a hydrogen ion-selective sensing material is reported. Bare nanoporous platinum oxides exhibit near-Nernstian behavior (e.g., −55 mV/pH in PBS), ignorable hysteresis, a short response time, and high precision, which are remarkably better than those of flat platinum oxides. The electrode potential of a nanoporous platinum oxide responds exclusively to hydrogen ion, which implies its usefulness as a solid-state pH sensor. In the present study, the performance of nanoporous platinum oxide was investigated and compared with that of IrO_x in terms of selectivity and the influences of ionic strength, temperature, complexing ligands, and surfactants. H₁-ePtO functions well as a pH-sensing solid-state material, and it is viewed as a promising alternative to IrO_x. Interference by redox couples was successfully suppressed by covering the H₁-ePtO surface with a protective layer, e.g., an electropolymerized polyphenol thin film. Since the nanoporous platinum oxide with such a protective layer is particularly suitable for miniaturization and micropatterning, our findings suggest its usefulness in applications such as solid-state pH sensors embedded in chip-based microanalysis systems.

pH sensors are essential components of analytical instruments, especially for chemical and biochemical analyses. Although many conventional pH sensors have been developed and a few of them are commercially available, the practical use of most pH sensors has been limited to the analyses of samples with large volumes. However, some emerging tools such as micro total analysis systems (μ -TAS)^{1–4} or pH microelectrodes^{3,5,6} increasingly require

new pH-sensitive materials, which are easy to fabricate and readily compatible with microsystems.

The solid-state pH sensors based on metal oxides have received considerable attention in recent decades in terms of the development of potential alternatives to the glass pH electrode for miniaturized systems, because metal oxides are mechanically robust, less sensitive to cation interference,⁷ and lend themselves to conventional patterning processes. Unfortunately, although most metal oxides are ostensibly suitable for solid-state pH sensors, only a few are acceptable in terms of practical criteria such as sensitivity, hysteresis, and the lack of interference by redox-active couples.⁷ IrO_x is the only material that has been recommended by a number of reports owing to its relatively low sensitivity to redox interference, low hysteresis, and potential stability over a wide pH range.^{5,8–11} To date, μ -TAS and pH microsensors have adopted IrO_x with a suitable protective layer.^{3,5} However, substitutes for IrO_x are rare at present.

Potentiometric pH sensors extract information about pH by measuring open circuit potential (E_{oc}), which is defined as the potential at which net current is zero. Ideally, a potentiometric sensor generating a stable response should have at least one nonpolarizable interface, on which any particular current does not produce further overpotential.¹² Intuitively, more reliable E_{oc} measurements are expected from less polarizable sensing interfaces. The equilibrium exchange current density, i_0 , is a quantitative criterion of polarizability according to Bockris and Reddy.¹² It is evident that the electrode/solution interface becomes proportionally less polarizable as i_0 climbs. The E_{oc} of metal/metal oxide is determined by the equilibrium between the metal/metal oxide and proton. It was previously reported that the E_{oc} of conducting oxides depends on the redox equilibrium as follows.⁷



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Since metal/metal oxide equilibria are basically established in confined surface reactions, i_0 should be proportional to the surface area. If the area of a flat electrode is not large enough to produce a sufficiently high i_0 , E_{oc} will be unstable. In addition to the enlargement of the electrode area, the geometric feature of mesopores may contribute to raise i_0 . It is presumable that the protons in the mesopores should be provided with more chances to collide with the active sites on the wall, leading to higher collision frequency than that at a flat planar surface. Consequently, it is predicted that the high surface roughness of nanoporous structures offers the benefit of low polarizability over conventional flat electrodes. A porous electrode, producing a larger i_0 than a flat electrode with an identical apparent area, is expected to respond more quickly, sensitively, and reproducibly to the presence of the large inner wall of the pores. It is interesting that such functional benefits may stem solely from structural modification of metal oxide surfaces.

In the present study, we employed hexagonally arranged cylindrical pores of platinum oxide (H_1 -ePtO) with diameter of 2.5 nm^{13,14} to examine the feasibility of using nanoporous structures for solid-state pH sensors. Reportedly flat platinum oxide (PtO is not the exact stoichiometric formula but an abbreviation standing for the various stoichiometric forms of platinum oxides and hydroxides) performs poorly as a pH-sensing material.⁷ The platinum/platinum oxide (Pt/PtO) equilibrium shows non-Nernstian behavior and suffers from a sluggish response and serious hysteresis. Moreover, redox couples such as $Fe(CN)_6^{3-/4-}$ disturb its E_{oc} more severely than those of the oxide semiconductors previously investigated. This is why flat platinum oxides have been excluded as candidates for potential pH sensors.

However, the nanoporous structure provides platinum electrodes with new opportunities. One of the examples was provided by our recent report, which demonstrated the enhancement of amperometric signals of a kinetically sluggish reaction due to the nanoporous electrode structure.^{15,16} In this report, we show the effects of nanoporous structure on potentiometric response, how nanoporous platinum oxide electrodes work as a solid-state pH sensor, which is potentially useful for miniaturized electrochemical systems such as detection units integrated on microfluidic chips.

EXPERIMENTAL SECTION

Reagents. All chemicals including octaethylene glycol monohexadecyl ether $C_{16}EO_8$ (Fluka), hydrogen hexachloroplatinate hydrate (Aldrich), *N*-2-hydroxyethylpiperazine-*N'*-2-ethanesulfonic acid (HEPES, Sigma), and tris(hydroxymethyl)aminomethane (Tris) hydrochloride (Sigma) were used without purification. Three kinds of surfactants were selected: *tert*-octylphenoxypolyethoxyethanol (Triton X-100, Sigma) as a neutral surfactant, sodium dodecyl sulfate (SDS, Fluka) as an anionic surfactant, and cetyltrimethylammonium chloride (CTAC, Aldrich) as a cationic surfactant. Ir wire (99.9%, 0.5 mm in diameter) was used to fabricate IrO_x for comparison purposes.¹⁷

Instruments. All electrochemical measurements were performed in a three-electrode system. The potentiostat employed in this work was a model CH660 from CH Instruments Inc. A calomel reference electrode saturated with KCl (SCE) and an Ag/AgCl (3 M KCl) was used as reference electrodes. The counter electrode was a platinum wire. The substrate electrode used for the nanoporous platinum film was a platinum disk of 1 mm in diameter. Another Pt disk was polished with 0.3- μ m alumina powder and used as a flat Pt electrode. E_{oc} measurements were carried out using a homemade multipotentiometer and five duplicate pH sensing electrodes versus a double-junction Ag/AgCl (Orion). A combination pH electrode (ROSS 8102, Orion) was used to check solution pHs during E_{oc} measurements.

Electrodeposition of Nanoporous Platinum. $C_{16}EO_8$ (0.42 g), distilled water (0.29 g), and hydrogen hexachloroplatinate hydrate (0.29 g) were mixed and heated to 80 °C; the mixture then became transparent and homogeneous. A polished platinum disk electrode (1 mm in diameter) was then inserted into this mixture, which was then cooled to room temperature. At this stage, the mixture becomes a highly viscous liquid crystalline material. Platinum deposition was carried out by applying a constant potential of -0.06 V versus Ag/AgCl until 25 mC had been passed. The resulting electrode was placed in distilled water for 1 h to extract the $C_{16}EO_8$, and this extraction procedure was repeated 3–4 times by replacing the water. The electrode was then electrochemically cleaned by cycling potential between +1.2 and -0.22 V versus Ag/AgCl in 1.0 M sulfuric acid, until reproducible cyclic voltammograms were obtained. It is believed that a hexagonal cylindrical porous platinum (H_1 -ePt) is formed during this procedure, as previously described.^{13,14} The surface areas of Pt electrodes were determined by measuring the area under hydrogen adsorption/desorption peaks in cyclic voltammograms at scan rate of 0.2 V s⁻¹ in 1.0 M aqueous sulfuric acid. A conversion factor of 210 μ C cm⁻² was used to calculate the electrode areas.¹⁸

Fabrication of Solid-State pH Sensors. A platinum oxide layer should be formed on the electrode surface for pH sensing. To do so, 0.6 V versus SCE was applied in PBS solution at pH 7.3 for 500 s. pH sensors with oxide layers on nanoporous and flat platinum electrodes in this report are referred to H_1 -ePtO and PtO-s, respectively.

The electrodes formed were coated with a polyphenol membrane using an electropolymerization technique, as previously described.^{19,20} In brief, a thin polyphenol layer was produced on a platinum oxide surface by performing five cyclic scans between +0.2 and +1.0 V versus Ag/AgCl at 2 mV s⁻¹ in a phosphate-buffered saline (PBS, pH 7.4) containing 10 mM phenol. The resulting H_1 -ePtO electrode covered with a polyphenol membrane is denoted as PPh/ H_1 -ePtO.

IrO_x layers were prepared using the conventional method for anodic iridium oxide film (AIROF) preparation.¹⁷ AIROFs were grown electrochemically on Ir wire by cycling potential between

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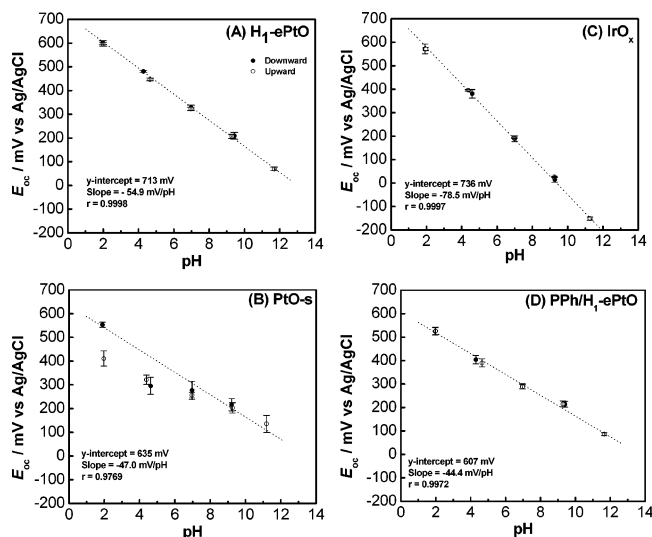


Figure 1. E_{oc} vs pH curves of (A) H_1 -ePtO, (B) PtO-s, (C) IrO_x , and (D) PPh/ H_1 -ePtO in unstirred and air-saturated PBS solutions, which were prepared by mixing 0.1 M H_3PO_4 and 0.1 M Na_3PO_4 containing 0.15 M NaCl. E_{oc} was recorded 60 s after the pH-sensitive electrodes were dipped into the solutions. pH was elevated from 2 to 12 (open circles) and then decreased to 2 (solid circles).

−0.2 and +1.3 V versus Ag/AgCl (200 cycles, 100 mV s^{−1}) in 1.0 M aqueous H_2SO_4 .

RESULTS AND DISCUSSION

Limitation of PtO as a Solid-State pH-Sensing Material.

According to Fog and Buck,⁷ PtO₂ does respond to pH changes but shows poor sensitivity, i.e., −46.7 mV/pH. Moreover, its reproducible linear dependence range is limited to between pH 5 and 10. They reported that PtO₂ exhibited more hysteresis than the other semiconducting oxides tested and that its performance is severely affected by redox couples in the solution.

For reliable pH sensors, it is widely accepted that metal oxide layers should not be dense and that they should be thick enough to maintain a high exchange current density. However, the problem is that platinum oxide is not easily formed as a thick layer. According to the review of Conway,²¹ a platinum oxide film is formed two-dimensionally with a surface coverage of less than 1 (monolayer of PtO) unless a potential more positive than 1.1 V versus the reversible hydrogen electrode (RHE) is applied for a long time. Moreover, there is a logarithmic correlation between platinum oxide growth and formation time.²² For example, the surface coverage of platinum oxide at 1.2 V versus RHE increases from 0.5 to 1 when the formation time is prolonged from 0.1 to 1000 s. If the applied potential is 1.3 V versus RHE, which is similar to the condition used to prepare platinum oxide in this report, the surface coverage would be less than 1.5 even after 1000 s. Thus, it is highly likely that the exchange current density, i_0 , for PtO-s would be too low to make E_{oc} reach equilibrium quickly and reproducibly. It is believed that this is the crucial reason flat platinum electrodes are unsuitable as pH sensors.

Performance of H_1 -ePtO as a pH Sensor. The pH responses of H_1 -ePtO in Figure 1A seems to be excellent compared with

Table 1. Slopes and y-Intercepts Values under Stirred and Unstirred Conditions

	slope/mV/pH		y-intercept/mV	
	unstirred ^a	stirred ^b	unstirred	stirred
H_1 -ePtO	−54.9	−54.8	713	713
PtO-s	−47.0	−48.4	635	635
IrO_x	−78.5	−78.8	736	737
PPh/ H_1 -ePtO	−44.4	−44.2	607	609

^a Data were acquired 60 s after the electrodes were immersed in unstirred solutions (Figure 1). ^b Data were obtained 30 s after stirring started.

those of PtO-s in Figure 1B in terms of (1) linearity, (2) hysteresis, and (3) precision. (1) H_1 -ePtO shows good linearity over a wide pH range from 2 to 12 whereas PtO-s deviated seriously from linearity. Moreover, the pH response of H_1 -ePtO exhibits near-Nernstian behavior with a slope of −55 mV/pH as shown in Figure 1A. (2) Hysteresis is so severe for PtO-s that the initial response at pH 2 (open circle) is not reproduced after exposure to solutions at higher pHs (solid circles). However, the platinum oxide on the surface of H_1 -ePt (H₁-ePtO) effectively suppressed hysteresis; in fact, it showed negligible hysteresis. (3) The narrow error bars in Figure 1A reflect the high precision of H_1 -ePtO, whereas wide error bars in Figure 1B indicate the poor reproducibility of PtO-s. Consequently, panels A and B of Figure 1 demonstrate that the introduction of a nanoporous surface remarkably improves the properties of platinum oxide as a solid-state pH sensor. In addition, its performance is comparable to that of the state-of-the-art IrO_x , as shown in Figure 1C.

For practical applications, interferences by redox couples, complexing agents, and surfactants should be eliminated. We screened a series of dense nonconducting polymers to identify one that is appropriate for preventing these interferences while preserving pH response. As a result, a polyphenol thin film was identified as a suitable protective layer, as it blocks most redox couples and allows only small species such as the hydrogen ion or hydrogen peroxide to permeate.^{19,20} The polyphenol layer was electropolymerized on the H_1 -ePtO by cycling the potential as described in the Experimental Section. The overall performance of the H_1 -ePtO as a pH sensor is affected by the polyphenol membrane (Figure 1D); however, at the expense of the decrease in the E_{oc} versus pH slope to −44 mV/pH, PPh/ H_1 -ePtO effectively suppresses the influence of interfering agents. This will be discussed in detail in a later section.

Stirring Effect. To investigate the effect of stirring, signals were collected while solutions were stirred and compared with those of unstirred solutions. Table 1 shows the slopes and y-intercepts of E_{oc} versus pH plots for the stirred and unstirred conditions. The E_{oc} of PtO-s was substantially affected by stirring, and the slope shifted by 1.4 mV/pH. On the other hand, H_1 -ePtO and PPh/ H_1 -ePtO responses showed no change regardless of stirring condition.

Stabilities of Platinum Oxide Electrodes. The reproducibility of E_{oc} with respect to pH was monitored for a month to check the stability of nanoporous Pt/PtO (H_1 -ePtO). The average of four E_{oc} values measured over 30 days using the same electrode was 0.367 V versus SCE with the standard deviation of 0.011 V at

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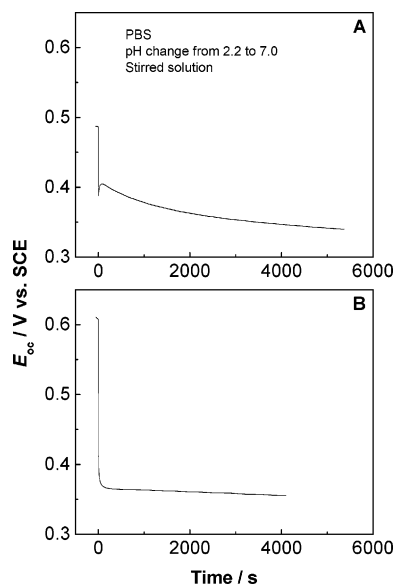


Figure 2. Chronopotentiometric responses of (A) PtO-s and (B) H₁-ePtO (rf 318) to a pH shift from 2.2 to 7.0. E_{oc} was recorded in aerated and stirred PBS solutions.

pH 7.3. This result demonstrates that the E_{oc} of H₁-ePtO was maintained without significant deterioration for longer than a month. On the other hand, the E_{oc} of PtO-s was so unstable that the standard deviation reached 0.032 V with the average value of 0.314 V under identical conditions.

Response Time. Figure 2 shows potential responses of H₁-ePtO and PtO-s to a pH shift from 2.2 to 7.0. The response of PtO-s was too slow to reach a steady potential even after 5000 s as displayed in Figure 2A. It is believed that this sluggish response is attributed to the low exchange current, i_0 , which makes it difficult for E_{oc} to be determined quickly by the equilibrium between H⁺ ions and surface-active sites. As a result, the E_{oc} of PtO-s is sensitive to impurities and deviates from Nernstian behavior.²³ In contrast, H₁-ePtO responds in less than 1 min ($t_{95\%}$ of ~30 s) to pH change and maintains a steady signal as shown in Figure 2B. This improvement presumably stems from H₁-ePtO surface reactions that overwhelm potential side reactions of impurity or redox couples.

Effects of Ionic Strength and Temperature. The extent of the dependence of E_{oc} on ionic strength is a practical pH sensor checkpoint. Figure 3 shows the variation of E_{oc} upon increasing the concentration of NaCl up to 100 mM in 1 mM sodium phosphate buffer, which was also used as a blank. The commercial glass electrode showed pH shifts from 7.00 to 6.97, 6.91, 6.86, 6.69, and 6.59 as the concentration of NaCl was increased from 0 to 1, 5, 10, 50, and 100 mM, respectively. A decrease in pH means an increase in E_{oc} , and E_{oc} values can be estimated in the absence of the ionic strength effect by calculation using the E_{oc} versus pH relationships shown in Figure 1 (Figure 3, dotted lines). Figure 3 shows that the E_{oc} of H₁-ePtO exhibits positive shifts, which are not as large as values expected if it is assumed that the ionic strength effect is absent. It is believed that this positive shift of E_{oc} reflects a pH decrease that occurs during NaCl addition and that positive shifts are lower than expected due to the effect of

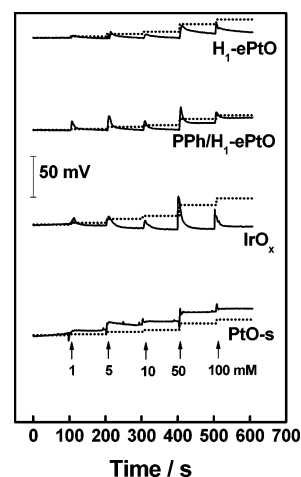


Figure 3. Experimental responses of H₁-ePtO, PPh/H₁-ePtO, IrO_x, and flat PtO to changes in ionic strength (solid lines) and the expected responses calculated from the data in Figure 1 in the absence of the ionic strength effect (dotted lines). Ionic strength was increased up to 100 mM by adding concentrated NaCl solution into 1 mM phosphate buffer solution at pH 7.0.

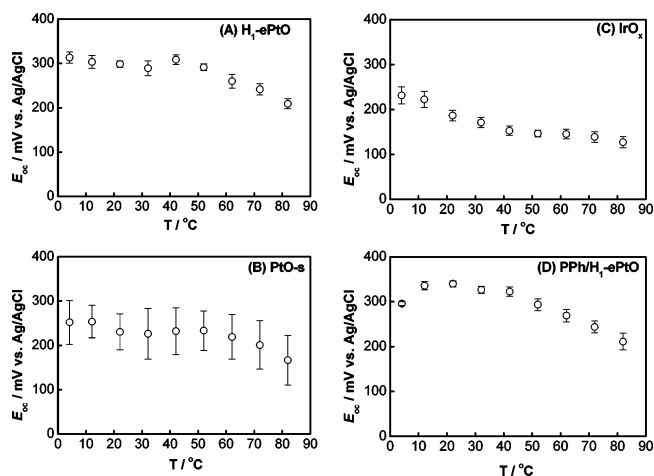


Figure 4. Effect of temperature on the E_{ocs} of (A) H₁-ePtO, (B) PtO-s, (C) IrO_x, and (D) PPh/H₁-ePtO in unstirred and air-saturated PBS solution at pH 7.0. E_{oc} values were recorded at 150 s after the electrodes were dipped into PBS solutions at given temperatures.

ionic strength. In contrast, PtO-s showed a positive shift in potential that was larger than theoretically expected. H₁-ePtO covered with a polyphenol membrane, PPh/H₁-ePtO, produced responses close to the theoretical ones, indicating little dependence on ionic strength. Interestingly, the E_{oc} of IrO_x barely followed pH changes as ionic strength was increased, demonstrating that it is significantly more sensitive to ionic strength than H₁-ePtO.

Figure 4 shows the dependence of E_{oc} on temperature. The E_{oc} values of the four electrodes tended to decrease as the temperature was elevated. This is not surprising because the slope of $-R/nF$ in the Nernst equation unambiguously reflects a negative temperature dependence. On the other hand, it should be noted that deviations in the E_{ocs} of H₁-ePtO, IrO_x, and PPh/H₁-ePtO are smaller than that of PtO-s and that PPh/H₁-ePtO shows a high degree of precision at around room temperature.

Cationic Interference. H₁-ePtO cation interference characteristics were investigated to evaluate the selectivity of H₁-ePtO

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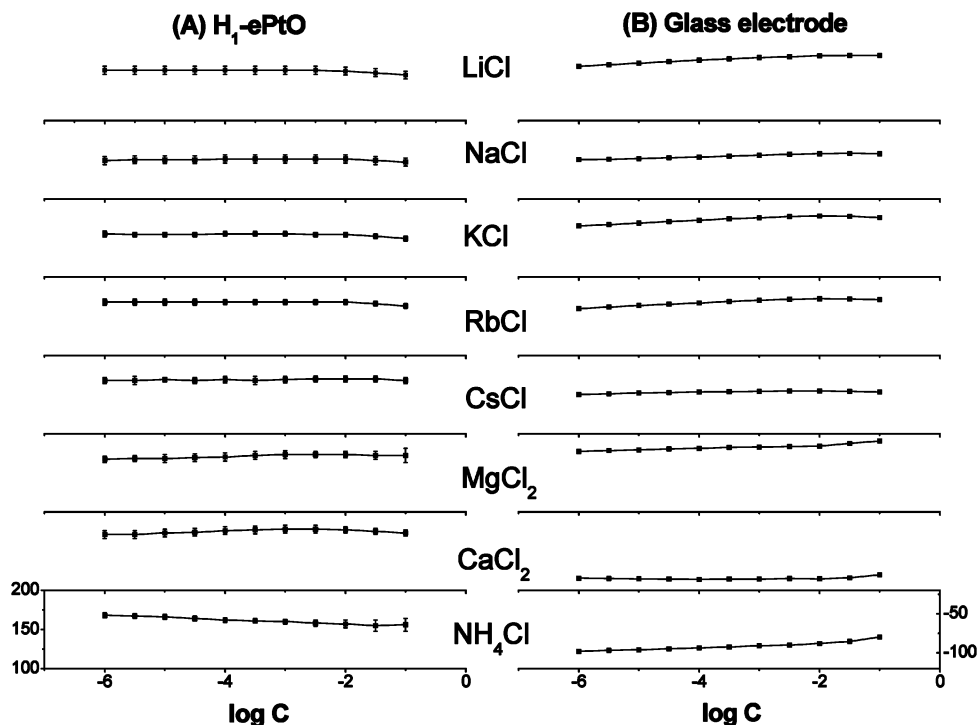


Figure 5. Responses of (A) H₁-ePtO and (B) glass electrodes to possible interfering cations (i.e., LiCl, NaCl, KCl, RbCl, CsCl, MgCl₂, CaCl₂, and NH₄Cl). Measurements were carried out in aerated and stirred Tris buffer solutions at pH 8.0, to which interfering ion solutions were added at intervals of 100 s.

as a H⁺ ion-selective electrode, as shown in Figure 5. H₁-ePtO responded only slightly to alkali metal, alkaline earth, and ammonium ions. Cation interference was observed at concentrations higher than $\sim 10^{-2}$ M. Figure 5 shows that the selectivities of H₁-ePtO to the H⁺ ion versus interfering cations are comparable to those of the glass electrode. In some cases H₁-ePtO exhibits better selectivity than the glass electrode, for example, in the low-concentration range for K⁺ and Li⁺.

Electrolyte Effect. Figure 6 shows the E_{oc} s that a couple of pH-sensing materials produce in various electrolyte solutions whose pH was not controlled intentionally. The E_{oc} values of H₁-ePtO in Figure 6A are marked with the calibration line in Figure 1A, which was determined in sodium phosphate/chloride solution. Since it was confirmed that cationic interference is negligible in Figure 5, the scattered points imply that anionic interference caused deviations from the calibration line. This is experimentally supported by deviations induced by NaI, NaBr, NaClO₄, NaNO₃, or Na₂SO₄, which indicate that significant interferences are caused by I⁻, Br⁻, ClO₄⁻, NO₃⁻, and SO₄²⁻. On the other hand, the deviations caused by H₂PO₄⁻, HPO₄²⁻, CO₃²⁻, and F⁻ were negligible. A comparison of PtO-s responses in Figure 6B and of H₁-ePtO in Figure 6A demonstrates that the nanoporous surface reduces interferences by electrolytes. H₁-ePtO was not inferior to IrO_x in this respect (Figure 6C), with the exception of interference by Br⁻. Figure 6D indicates that the presence of a polyphenol membrane as a protective layer modifies the interference pattern of H₁-ePtO.

Effect of Complexing Agents. Sometimes pH measurements must be made in solutions containing various complexing ligands, which may be adsorbed onto the solid/electrolyte interface and produce potential changes. Figure 7 shows the responses of tested pH electrodes in the presence of a variety of organic ligands. H₁-

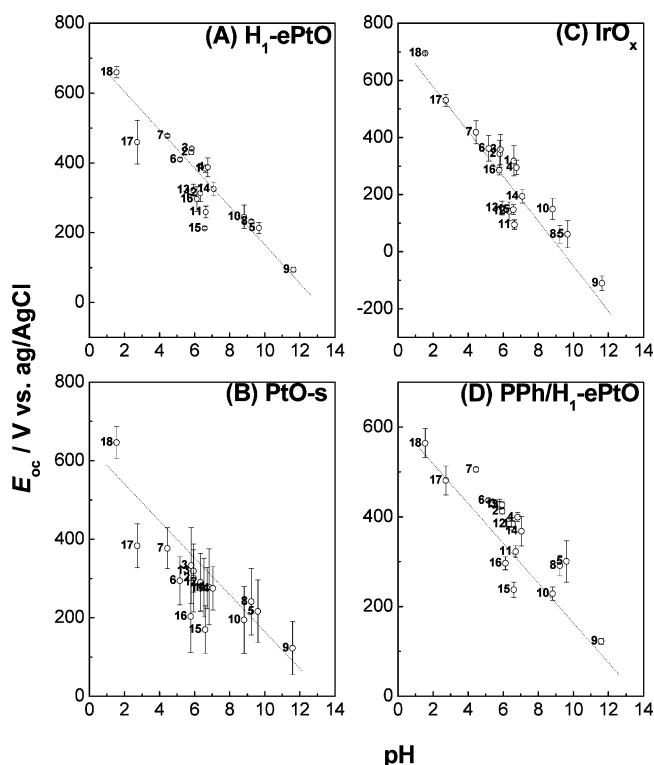


Figure 6. Effect of various ions on the E_{oc} of (A) H₁-ePtO, (B) PtO-s, (C) IrO_x, and (D) PPh/H₁-ePtO. Measurements were conducted in 0.1 M NaCl (1, pH 6.6), KCl (2, pH 5.8), MgCl₂ (3, pH 5.8), CaCl₂ (4, pH 6.8), LiCl (5, pH 9.7), NH₄Cl (6, pH 5.2), NaH₂PO₄ (7, pH 4.5), Na₂HPO₄ (8, pH 9.2), Na₂CO₃ (9, pH 11.6), NaHCO₃ (10, pH 8.8), NaClO₄ (11, pH 6.6), NaNO₃ (12, pH 6.3), Na₂SO₄ (13, pH 5.9), NaF (14, pH 7.1), NaI (15, pH 6.6), NaBr (16, pH 6.1), CuCl₂ (17, pH 2.7), and FeCl₃ (18, pH 1.5). Calibration lines determined in PBS solution (Figure 1) were inserted for comparison.

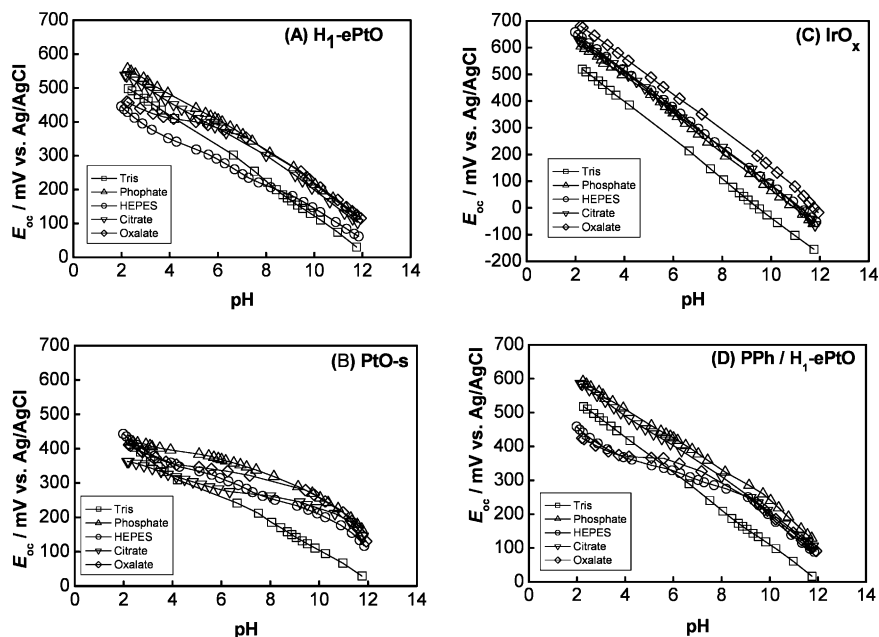


Figure 7. pH responses of (A) H_1 -ePtO, (B) PtO-s, (C) IrO_x , and (D) PPh/ H_1 -ePtO in stirred 0.15 M NaCl solutions containing 20 mM phosphate, oxalate, citrate, HEPES, or Tris. pH was adjusted by adding appropriate amounts of 0.1 M NaOH or HCl and was measured with using a glass electrode.

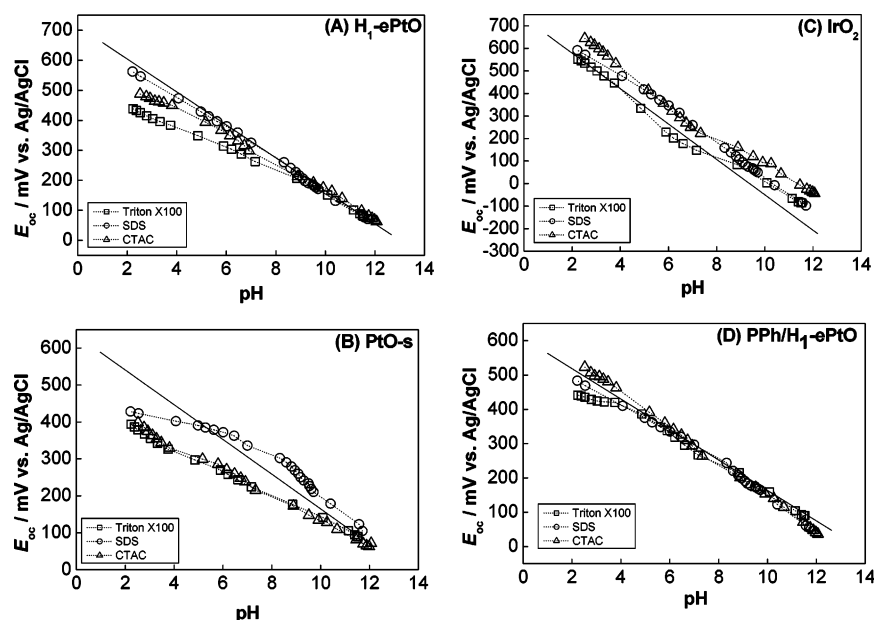


Figure 8. pH responses of (A) H_1 -ePtO, (B) PtO-s, (C) IrO_x , and (D) PPh/ H_1 -ePtO in the presence of surfactants. The solutions are 0.15 M aqueous NaCl containing 1wt % Triton X100 (squares), SDS (circles), or CTAC (triangles). Calibration lines determined in PBS solution (Figure 1) were inserted for comparison.

ePtO gave tolerable linearity in the presence of Tris, phosphate, and citrate. However, H_1 -ePtO showed a significant deviation from linearity in the presence of oxalate or HEPES, especially in acidic conditions. It is noteworthy that the interference observed in the case of PtO-s was so serious that it almost lost its pH-sensing ability as found in Figure 7B. The nanoporous structure improved pH response linearity in the presence of complexing agents, although its linearity was not as good as that of IrO_x in Figure 7C. Polyphenol layer did not further improve the linearity of H_1 -ePtO as shown in Figure 7D. It appears that complexing agents examined during this study were too small to be effectively excluded by the polyphenol.

Effect of Surfactants. Like complexing agents, surfactants are also commonly encountered in environmental or biological analysis. Moreover, surfactants are expected to severely affect the E_{oc} of solid-state pH sensors. Figure 8A indicates that H_1 -ePtO produces linear pH responses in the presence of the surfactants such as Triton X100, SDS, and CTAC and that SDS had little influence on E_{oc} , whereas CTAC and Triton X100 reduced the slope. pH response linearity of PtO-s was disrupted, as shown in Figure 8B, and contrasts with the good linearity of H_1 -ePtO. Figure 8C shows that the E_{oc} of IrO_x shifts significantly in the presence of surfactants. The interferences by surfactants were somewhat suppressed by the polyphenol layer as shown in Figure 8D, which

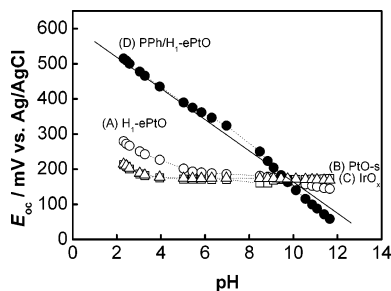


Figure 9. pH responses of (A) H₁-ePtO, (B) PtO-s, (C) IrO_x, and (D) PPh/H₁-ePtO in 0.15 M NaCl containing the redox couple, 1 mM Fe(CN)₆^{3-/4-}. The pH of the solution was changed from 2 to 12 by adding 1.0 M HCl or NaOH. Calibration line determined in PBS solution (Figure 1D) was inserted for comparison.

is supposedly attributed to their size being larger than the complexing agents examined.

Effect of Redox Couples in Solution. Figure 9 shows that the E_{oc} values of PtO-s and IrO_x are highly sensitive to the presence of the Fe(CN)₆^{3-/4-} redox couple. The E_{oc} values of PtO-s and IrO_x were predominantly determined by the redox equilibrium of the Fe(CN)₆^{3-/4-} couple rather than by the H⁺ ion equilibrium. This phenomenon is commonly observed for most metal oxides.⁷ Moreover, despite the excellent performance of IrO_x as a solid-state pH sensor, its applications are seriously restricted in the presence of redox couples such as Fe(CN)₆^{3-/4-}.^{5, 7}

On the other hand, the responses of H₁-ePtO differed from those of PtO-s or IrO_x. Although E_{oc} is still seriously affected by the Fe(CN)₆^{3-/4-} couple, enhancement in the contribution of Pt/PtO is notable in low pH region. This result implies that the contribution of the surface equilibrium on nanoporous Pt/PtO to E_{oc} is not negligible. This is not surprising because it is evident that the exchange current of nanoporous Pt/PtO is proportional to the surface area and H⁺ ion-dependent equilibria become important at a low pH. Therefore, the nanoporous structure suppresses the influence of Fe(CN)₆^{3-/4-} on E_{oc} , although there remains room for further improvement.

Interference by Fe(CN)₆^{3-/4-} can be effectively reduced by a protective film on the nanoporous Pt/PtO surface. Figure 9 shows that H₁-ePtO coated with polyphenol (PPh/H₁-ePtO) exhibits near-Nernstian behavior. It is believed that the polyphenol rejects Fe(CN)₆^{3-/4-} but that it allows H⁺ ions to selectively permeate the membrane. Moreover, the polyphenol layer does not inhibit the ability of H₁-ePtO to act as a pH sensor.

This result indicates that PPh/H₁-ePtO is a promising practical pH sensor. It is worth noting that all systems are affected to some extent by redox couples. Even though IrO_x is coated with a thick Nafion layer, it reportedly behaves as a redox electrode rather than pH electrode.⁵ And platinum is more widely used metal in micromachining lines than iridium. In these respects, the developed PPh/H₁-ePtO system is expected to provide practical solutions in various electrochemical applications, for example, as a chemical/biosensor in micro total analysis systems. The electrodes can be produced quickly, easily, and reproducibly and thus favors mass production. Moreover, PPh/H₁-ePtO can be patterned on microchips. It is believed that miniaturized analysis systems, such as pH-sensing units integrated into microfluidic chips, have a number of potential applications.

CONCLUSION

Nanoporous structures can remarkably improve the intrinsic drawbacks of platinum when it is used to construct pH-sensitive electrodes. It should be noted that thin-layer or even monolayer metal oxides can be used as pH sensors by introducing extremely minute pores in the surface. Furthermore, the same principle could be applied to other metal oxides, which opens up lots of possibilities for the development of practical pH sensors.

ACKNOWLEDGMENT

This work was supported by the Korea Science and Engineering Foundation through the Advanced Biometric Research Center.

Received for review June 2, 2005. Accepted September 26, 2005.

AC050968J