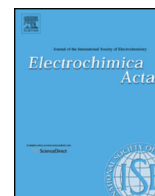


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pH Sensors Using 3d-Block Metal Oxide-Coated Stainless Steel Electrodes

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ABSTRACT

The 3d-block metal oxide-coated SUS304 electrodes (MO_x/SUS , $M = \text{Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu}$ and Zn) were prepared using the sol-gel dip-coating method in order to develop novel pH sensors. MO_x/SUS electrodes showed a pH sensitivity of 88–100%, a pH repeatability of 0.1–0.6 in pH units and an initial pH response time of approximately 1 sec. The pH sensitivities of the SUS (as-received) and SUS-500 (heated at 500 °C) were 91% and 94%, respectively. Therefore, it appeared that the pH sensitivity of the MO_x/SUS electrode was affected by the underlying materials (SUS substrate and its oxide layer) as well as by the outer MO_x films. All of the MO_x/SUS electrodes showed much shorter initial pH response time than a commercial glass electrode (14 sec). In particular, $\text{Co}_3\text{O}_4/\text{SUS}$ and CuO/SUS electrodes were considered candidates for disposable pH electrodes, pH microelectrodes and tube and needle-type pH electrodes for novel pH sensors as a result of their favorable pH sensitivity, pH repeatability and initial pH response time.

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1. Introduction

Commercially available lithium silicate-based pH glass electrodes possess ideal Nernstian responsivity (pH sensitivity) independent of redox interferences, a short balancing time of electrical potential (pH response time), high repeatability and a long lifetime, as well as high chemical durability over a wide pH range. However, they have several drawbacks for various industrial applications because potentiometric measurement of pH using glass electrodes is often influenced by several factors. Therefore, there is an increasing need for alternative pH electrodes. New technologies for pH measurement such as metal/metal oxide, ion sensitive field-effect transistors (ISFET), fiber-optical techniques, nanotechniques and conducting polymer techniques have been extensively developed thus far [1]. Techniques superior to potentiometric measurement of pH using glass electrodes have not been established yet because of lower chemical durability and higher cost compared to pH glass electrodes.

The problem of uncertainty evaluation in routine pH measurement by glass electrodes has been given considerable attention in recent years, and relevant components of the uncertainty have been investigated through different approaches. Among these

uncertainty components are those arising from the calibration procedure, the quality of calibration standards, temperature effects, drift of the measurement system and others (the residual liquid junction potential, i.e., the difference in junction potentials between measurements with the test and standard solutions) [2]. In fact, important customer issues with pH measurements include a decrease in pH sensitivity and an increase in pH response time (measuring time), which primarily result from the contamination of the responsive glass membrane and liquid junction and from a change in the concentration of the internal liquid. To avoid these issues, customers have to continually maintain their pH glass electrodes. This can be troublesome, especially in industrial uses, where it is not easy to remove the accumulated stain from pH glass electrodes.

For this reason, we have developed novel pH glass electrodes, such as $\text{TiO}_2\text{-P}_2\text{O}_5$ (TP) glasses, with a self-cleaning property based on photocatalytic activity and photo-induced hydrophilicity [3]. Additionally, $\text{Fe}_2\text{O}_3\text{-Bi}_2\text{O}_3\text{-B}_2\text{O}_3$ (FeBiB) glasses have been developed as novel pH-responsive glasses with an anti-fouling property based on their hydrophobicity [4,5]. Such novel lithium-free, non-silicate pH-responsive glasses are expected to show a short pH response time because they are a new type of pH glass electrodes based on “electronic conduction” that differs from the “ionic conduction” existing in commercial lithium silicate glasses.

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The use of glass sensors is inappropriate for in vivo biomedical, clinical or food applications even if they are maintenance free because of the brittleness of glass and the difficulty in measuring small volumes [6]. As the next step, we aim for the development of disposable pH electrodes [7–9], pH microelectrodes [10–15] and tube and needle-type pH electrodes, which are suitable for pH measurements with a narrow region and depth profile and in vivo and in situ measurements. Metal-based pH electrodes are considered suitable for this purpose. They do not require an amplifier, unlike with pH glass electrodes; therefore, metal-based pH electrodes allow to downsize and keep the cost down for the pH meter.

Although polymers are often used as a substrate, metal electrodes such as Au are needed [13,15–18]. Stainless steel is a strong candidate for a metal electrode in terms of the cost (especially for disposable pH electrodes) and the suitable chemical durability. Although there has been a report of stainless-steel-based pH electrodes [19], it has not been followed by subsequent research. In the literature, it is described that the oxidized SUS304 electrode was Nernstian pH-responsive, but the pH response was affected by Cl^- ions. This means that further modification of the SUS304 electrode is necessary. Therefore, metal oxide coatings [20–22] are required to give pH-responsive sites with high H^+ ion selectivity and to protect the stainless steel.

Metal oxides such as PtO_2 [23], IrO_2 [1,12–18,23,24], RuO_2 [10,23,25–30], OsO_2 [23], Ta_2O_5 [23], TiO_2 [23,31,32], MnO_2 [23,33], Co_3O_4 [34], NiO [6], CuO [16], ZnO [35], WO_3 [10] and CeO_2 [8] have been investigated as pH-responsive films instead of pH glass electrodes thus far. Although most of the research has focused on IrO_2 and RuO_2 electrodes, these metal oxides are too expensive for commercial use. Recently, there have been several studies on more inexpensive pH sensors using a binary system such as $\text{IrO}_x\text{-TiO}_2$ [24], $\text{RuO}_2\text{-SnO}_2$ [29] and $\text{RuO}_2\text{-Ta}_2\text{O}_5$ [30]. However, IrO_2 - and RuO_2 -based compounds often show a non-ideal Nernstian pH response such as a super-Nernstian pH response [10,12,15,17,23,24,27] or a sub-Nernstian pH response [13,24,25,29,30]. Conversely, d-block metal oxides such as TiO_2 , MnO_2 , Co_3O_4 , NiO , CuO , ZnO and WO_3 are more advantageous with regards to cost. Because CuO-SiO_2 [20], TiO_2 [21] and TiO_2/ZnO [22] were coated on stainless steel via the sol-gel method for corrosion protection, 3d-block metal oxide-coated stainless steel electrodes are a candidate for a new, inexpensive pH electrode. However, as far as we know, there have not been systematic studies on 3d-block metal oxide-coated pH electrodes.

In the present study, 3d-block metal oxide-coated SUS304 electrodes (MO_x/SUS , $\text{M} = \text{Sc}$, Ti , V , Cr , Mn , Fe , Co , Ni , Cu and Zn) were prepared using the sol-gel dip-coating method in order to develop the novel pH sensors. Additionally, the pH responsivity

(pH sensitivity, pH repeatability and the initial pH response time) of the MO_x/SUS electrodes was investigated.

2. Experimental

The 3d-block metal oxide-coated SUS304 electrodes (MO_x/SUS , $\text{M} = \text{Sc}$, Ti , V , Cr , Mn , Fe , Co , Ni , Cu and Zn) were prepared using the sol-gel dip-coating method. $\text{Sc}(\text{NO}_3)_3 \cdot 4\text{H}_2\text{O}$ (99.9%, Kojundo Chemical Lab. Co., Ltd., Sakado, Japan), $\text{Ti}(\text{O}-i\text{-C}_3\text{H}_7)_4$ (1st grade, Wako Pure Chemical Industries, Ltd., Osaka, Japan), $\text{C}_{10}\text{H}_{14}\text{O}_5\text{V}$ (Extra pure grade, Tokyo Chemical Industry Co., Ltd., Tokyo, Japan), $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Guaranteed reagent grade, Nacalai Tesque, Inc., Kyoto, Japan), $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Guaranteed reagent grade, Nacalai Tesque, Inc., Kyoto, Japan), $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Guaranteed reagent grade, Wako Pure Chemical Industries, Ltd., Osaka, Japan), $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Guaranteed reagent grade, Nacalai Tesque, Inc., Kyoto, Japan), $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Guaranteed reagent grade, Nacalai Tesque, Inc., Kyoto, Japan), $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (Guaranteed reagent grade, Wako Pure Chemical Industries, Ltd., Osaka, Japan) and $\text{Zn}(\text{OCOCH}_3)_2 \cdot 2\text{H}_2\text{O}$ (Guaranteed reagent grade, Nacalai Tesque, Inc., Kyoto, Japan) were used as metal sources. $\text{CH}_3\text{O}(\text{CH}_2)_2\text{OH}$ (Guaranteed reagent grade, Nacalai Tesque, Inc., Kyoto, Japan) was used as a solvent with a metal: $\text{CH}_3\text{O}(\text{CH}_2)_2\text{OH}$ molar ratio of 1:40. HNO_3 (Guaranteed reagent grade, Nacalai Tesque, Inc., Kyoto, Japan) for the preparation of TiO_2 and V_2O_5 , $\text{C}_5\text{H}_8\text{O}_2$ (Guaranteed reagent grade, Nacalai Tesque, Inc., Kyoto, Japan) for the preparation of Fe_2O_3 and $\text{H}_2\text{N}(\text{CH}_2)_2\text{OH}$ (Guaranteed reagent grade, Nacalai Tesque, Inc., Kyoto, Japan) for the preparation of ZnO were added to $\text{CH}_3\text{O}(\text{CH}_2)_2\text{OH}$. Metal sources except metal nitrates, additives to $\text{CH}_3\text{O}(\text{CH}_2)_2\text{OH}$ and other molar ratios were used, taking into consideration some of the references [36–39] and our preliminary experiments. The composition of the coating solutions and the flowchart for the preparation of 3d-block metal oxide-coated stainless steel electrodes (MO_x/SUS) are listed in Table 1 and Fig. 1, respectively.

As a stainless steel substrate, SUS304 (Nilaco Corporation, Tokyo, Japan) was used. A SUS304 substrate with $33 \text{ mm} \times 80 \text{ mm} \times 0.1 \text{ mm}$ was immersed into a coating solution and pulled up at a rate of 0.5 mm/sec. The film was pre-heated at 500°C for 10 min. After this procedure was repeated three times, the film was heated at 500°C for 24 h.

Potentiometric measurements for the MO_x/SUS electrodes was carried out at 25°C at time intervals of 3 s and 0.5 s using a pH meter F-73 (HORIBA, Ltd., Kyoto, Japan) and a portable multi logger ZR-RX20 (OMRON Corp., Kyoto, Japan) equipped with a handmade cell with a MO_x/SUS with a thickness of 0.1 mm (or lithium silicate glass (HORIBA, Ltd., Kyoto, Japan) with a thickness 1.0 mm for comparison). The portable multi logger ZR-RX20 was used for

Table 1
Compositions of the coating solutions (molar ratio).

Sample name	Metal source (molar ratio)		$\text{CH}_3\text{O}(\text{CH}_2)_2\text{OH}$	Additive	
$\text{Sc}_2\text{O}_3/\text{SUS}$	$\text{Sc}(\text{NO}_3)_3 \cdot 4\text{H}_2\text{O}$	1	40		
TiO_2/SUS	$\text{Ti}(\text{O}-i\text{-C}_3\text{H}_7)_4$	1	40	HNO_3	0.1
				H_2O	1
$\text{V}_2\text{O}_5/\text{SUS}$	$\text{C}_{10}\text{H}_{14}\text{O}_5\text{V}$	1	80	HNO_3	1
$\text{Cr}_2\text{O}_3/\text{SUS}$	$\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	1	40		
$\text{Mn}_2\text{O}_3/\text{SUS}$	$\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	1	40		
$\text{Fe}_2\text{O}_3/\text{SUS}$	$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	1	40	$\text{C}_5\text{H}_8\text{O}_2$	2
$\text{Co}_3\text{O}_4/\text{SUS}$	$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	1	40		
NiO/SUS	$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	1	40		
CuO/SUS	$\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$	1	40		
ZnO/SUS	$\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$	1	40	$\text{H}_2\text{NCH}_2\text{CH}_2\text{OH}$	1

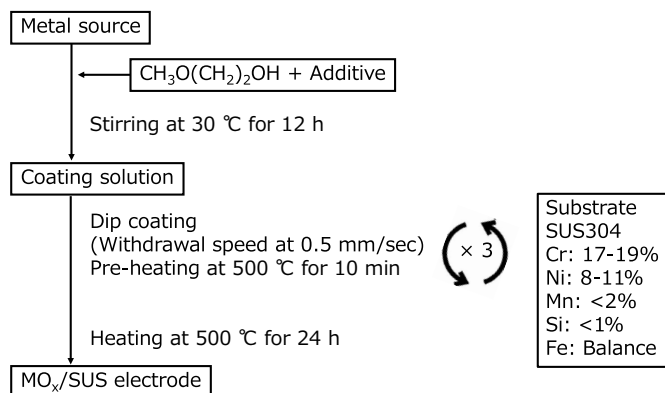


Fig. 1. Flowchart for the preparation of MO_x/SUS electrodes.

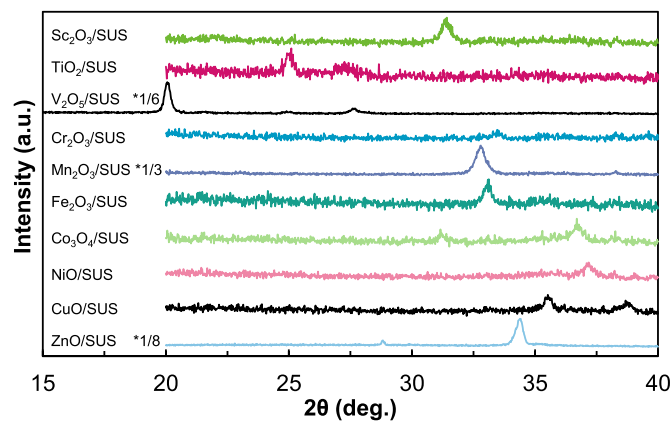


Fig. 2. XRD patterns of MO_x/SUS electrodes.

Table 2
pH response time and initial pH response time of $\text{Co}_3\text{O}_4/\text{SUS}$ and glass electrodes.

Sample name	pH response time (sec) $ E_{\text{t}+3}-E_{\text{t}} < 1.5$	Initial pH response time (sec) $E < 0.1(E_4-E_7)$
$\text{Co}_3\text{O}_4/\text{SUS}$	9	1.0
Glass electrode (HORIBA)	27	14.0

determination of initial pH response time as will be given in Tables 2 and 3 and Fig. 4. The details of the pH responsivity (pH sensitivity, pH repeatability and pH response time) were described in Refs. [3–5]. The precipitated crystal phases were determined from XRD patterns measured using an Ultima IV instrument (Rigaku, Tokyo, Japan).

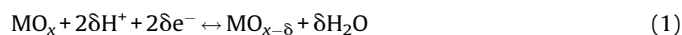
3. Results and discussion

Fig. 2 shows the XRD patterns of MO_x/SUS electrodes. Most of the metal oxides used in each sample name were detected as single phase. In this figure, the intensity of the XRD patterns of $\text{V}_2\text{O}_5/\text{SUS}$, $\text{Mn}_2\text{O}_3/\text{SUS}$ and ZnO/SUS were drawn on a reduced scale. Although a small amount of V_4O_9 ($\text{V}_2\text{O}_{4.5}$), which was observed at approximately $2\theta = 28^\circ$, coexisted with V_2O_5 , $\text{V}_2\text{O}_5/\text{SUS}$ was nominally used as a sample name.

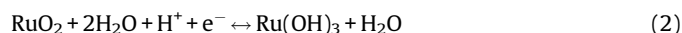
When a metal oxide is exposed to a solution, several chemical reactions will occur on the surface of the oxide such as hydration, dissolution, hydrolysis and dissociation [29]. According to the site-

binding theory, the surface groups $-\text{O}^-$, $-\text{OH}$ and $-\text{OH}_2^+$ are developed for the majority of oxides after immersion in an aqueous solution. Protons and hydroxide ions from the solution are attracted to oxygen ions from the metal oxide crystal lattice and to the surface cations, respectively. This results in covering of the metal oxide by hydroxide groups. The created metal hydroxide groups can donate a proton to the solution and form a negative surface group ($-\text{O}^-$) or accept a proton from the solution, converting into a positive surface group ($-\text{OH}_2^+$).

Fog and Buck proposed five possible interpretations for the pH response mechanism of metal oxides, with the most accepted theory being oxygen intercalation [23,25,27,28]. The oxygen intercalation mechanism is represented by the following equilibrium reaction:



where δ is the intercalation of interstitial oxygen, MO_x is a higher valence metal oxide and $\text{MO}_{x-\delta}$ is a lower valence metal oxide. As for Ru_2O_3 electrodes, the pH response mechanism is governed by a redox equilibrium between two insoluble ruthenium compounds, which is governed by the following reaction [25,27,28].



At present, we generalized the reaction for the 3d-block metal oxides (MO_x) as follows, where MO_x is a higher valence metal oxide and $\text{MO}_{x-\delta}(\text{OH})_\delta$ is a partially hydrolyzed lower valence metal oxide.

Table 3
pH sensitivity, pH repeatability and initial pH response time of MO_x/SUS electrodes.

Sample name	pH sensitivity (%) @pH 4–9	pH repeatability (pH) @pH 7	Initial pH response time (sec) @pH 7
$\text{Co}_3\text{O}_4/\text{SUS}$	99.8	0.13	1.0
$\text{Mn}_2\text{O}_3/\text{SUS}$	98.3	0.18	1.5
$\text{Cr}_2\text{O}_3/\text{SUS}$	98.1	0.21	0.5
CuO/SUS	97.9	0.05	1.0
ZnO/SUS	97.5	0.34	2.0
$\text{V}_2\text{O}_5/\text{SUS}$	95.5	0.06	1.0
TiO_2/SUS	95.0	0.20	1.0
$\text{Fe}_2\text{O}_3/\text{SUS}$	94.5	0.28	1.0
$\text{Sc}_2\text{O}_3/\text{SUS}$	87.9	0.22	1.0
NiO/SUS	87.7	0.62	1.0
SUS	90.9	0.44	1.0
SUS-500	94.1	0.17	1.0
Glass electrode (HORIBA)	99.2	0.13	14.0

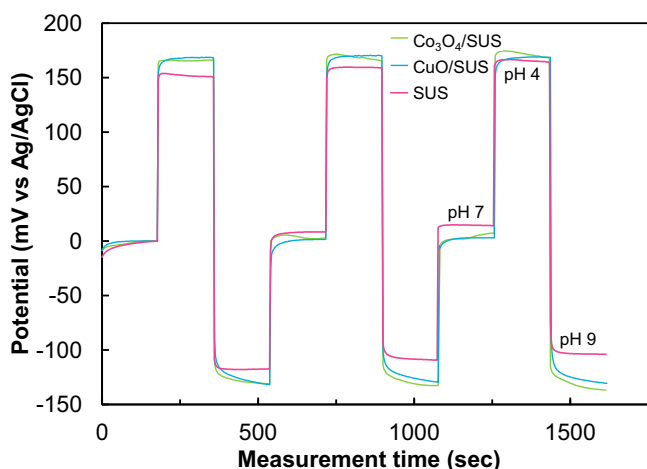


Fig. 3. Change in potential with measurement time for Co₃O₄/SUS, CuO/SUS and SUS electrodes in pH 7, pH 4 and pH 9 buffer solutions as a representative example.

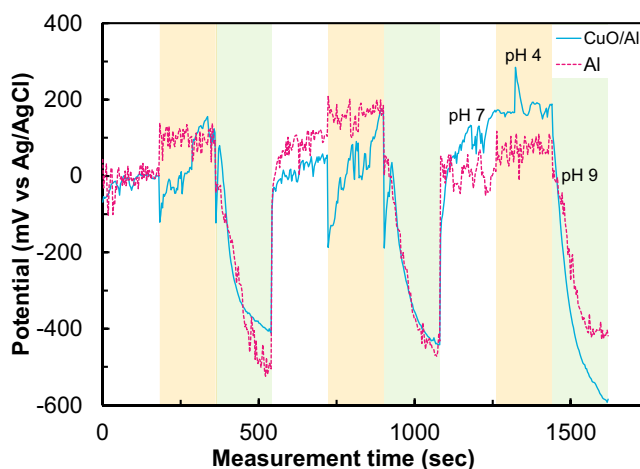
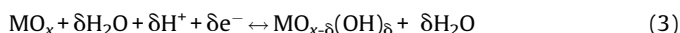


Fig. 5. Change in potential with measurement time for CuO/Al and Al electrodes in pH 7, pH 4 and pH 9 buffer solutions.



Because the standard solutions do not contain M species, the only transient electron transfer may occur at the MO_x/SUS interface according to reaction (3), analogous with Ref. [33]. This can be balanced by the insertion-removal of protons at the film/solution interface given by the same reaction.

Fig. 3 indicates the change in potential with measurement time for Co₃O₄/SUS, CuO/SUS and SUS electrodes in pH 7, pH 4 and pH 9 buffer solutions as a representative example. It is seen from this figure that SUS shows a relatively good pH response for pH 7, pH 4 and pH 9 buffer solutions. Co₃O₄/SUS and CuO/SUS electrodes show a potential curve with a larger amplitude than that of the SUS electrode. This means that these electrodes have higher pH sensitivity than the SUS electrode.

Fig. 4 shows (a) the initial potential curves of Co₃O₄/SUS and glass electrodes for the pH 7 buffer solution and (b) an enlarged view. The conventional “pH response time” [3] estimated from Fig. 4(a) of Co₃O₄/SUS and glass electrodes was 9 sec and 27 sec, respectively (Table 2). These values are different from the actual impression from Fig. 4(a). The conventional “pH response time”, which is the time required to give a stable potential for 3-sec intervals, is unsuitable in the case of a very short response time.

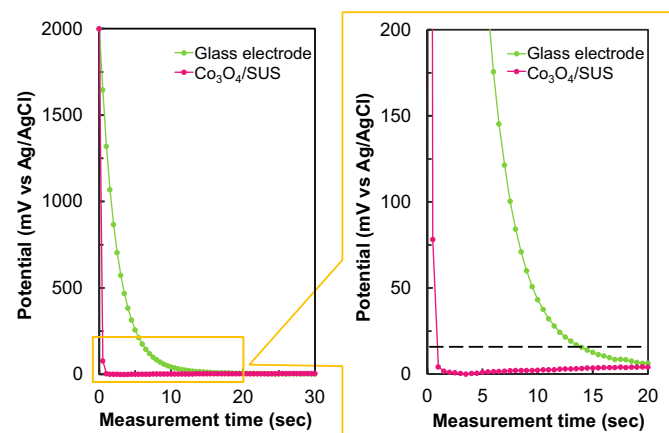


Fig. 4. (a) Initial potential curves of Co₃O₄/SUS and glass electrodes for pH 7 buffer solution and (b) enlarged view.

Therefore, another pH response time that referred to the “initial pH response time” was introduced. This is time required to obtain 90% of E₄–E₇ in a 0.5-sec interval, where E₄ and E₇ are a stable potential after 180 sec for pH 4 and pH 7 buffer solutions, respectively. The initial pH response time for Co₃O₄/SUS (1.0 sec) is much faster than that of a commercial glass electrode (14.0 sec) (Table 2).

Table 3 summarizes the pH sensitivity, pH repeatability and initial pH response time of the MO_x/SUS electrodes. Most of the MO_x/SUS electrodes showed higher pH sensitivities (the second column in Table 3) (88–100%) than that of SUS (91%). When the MO_x/SUS electrodes were heated at 500 °C for 24 h for the preparation of MO_x films, an oxide layer such as Fe₂O₃ [40] formed at the MO_x films/SUS substrate interface. The pH sensitivity of SUS-500 (heated at 500 °C for 24 h) was measured to reveal the effect of an oxide layer on the pH sensitivity. It should be noted that the pH sensitivity of SUS-500 is higher (94%) than that of SUS (91%). This means that an oxide layer on the SUS surface has higher pH sensitivity than that of the SUS substrate. There is further information on the effect of underlying materials (SUS substrate and its oxide layer) on pH response. Fig. 5 shows the change in potential with measurement time for CuO/Al and Al electrodes in pH 7, pH 4 and pH 9 buffer solutions. Both CuO/Al and Al electrodes show the unstable and super-Nernstian potential in the same way. If the pH sensitivity of the MO_x/SUS electrodes is determined only by MO_x films, CuO/Al should show a stable and Nernstian potential similar to that of CuO/SUS in Fig. 3. Thus, it appeared that the observed pH sensitivity of MO_x/SUS electrodes is affected by the underlying materials (metal substrate and its oxide layer) as well as by the outer MO_x films.

The pH sensitivity of the MO_x/SUS was classified into three categories: (1) 88% for Sc₂O₃/SUS and NiO/SUS electrodes; (2) 95–96% for V₂O₅/SUS, TiO₂/SUS and Fe₂O₃/SUS electrodes; and (3) 98–100% for Co₃O₄/SUS, Mn₂O₃/SUS, Cr₂O₃/SUS, CuO/SUS and ZnO/SUS electrodes. In category (1), MO_x films have lower pH sensitivities than the oxide layer of SUS. In category (2), the pH sensitivity of MO_x films is comparable to that of the oxide layer of SUS. In category (3), MO_x films have higher pH sensitivities than the oxide layer of SUS. In category (1), the reaction according to Eq. (3) is unlikely for NiO and Sc₂O₃, which have stable divalent and trivalent metal cations, respectively. Therefore, they may not show high pH sensitivity. In category (2), it is reasonable that the pH sensitivity of the Fe₂O₃/SUS electrode (95%) is close to that of the SUS-500 electrode (94%), which has an outer layer such as Fe₂O₃ on

the SUS surface. V_2O_5/SUS and TiO_2/SUS electrodes have a possible pH response according to Eq. (3). It appeared that the pH sensitivity of Co_3O_4/SUS , Mn_2O_3/SUS , Cr_2O_3/SUS , CuO/SUS and ZnO/SUS electrodes (98–100%) is dominated by the pH sensitivity of the MO_x films. Although ZnO with a stable divalent is in category (3), there is no known explanation for this discrepancy currently. Additionally, it is unexplained that the order of pH sensitivity is not systematic as for valence of 3d-block elements, the number of electrons occupying d-orbitals and so on. This may be the result of several parameters, such as penetration into the oxide layer on the SUS by buffer solution because of the porous nature (extrinsic factors) and electrical conductivity (intrinsic factors) of the films.

Most of the SUS electrodes exhibited good pH repeatability (0.1–0.6 in pH units), as shown in the third column in Table 3. Especially, Co_3O_4/SUS , CuO/SUS and V_2O_5/SUS electrodes exhibited high pH repeatability (0.1 in pH units) comparable to that of a commercial glass electrode. All of the SUS electrodes exhibited much shorter initial pH response time (approx. 1 sec) than the commercial glass electrode (14 sec), as shown in the fourth column in Table 3. This may be attributed to the much lower electrical resistivity of the SUS electrode compared to that of commercial glass electrode. Thus, Co_3O_4/SUS and CuO/SUS electrodes exhibited favorable pH sensitivity, pH repeatability and initial pH response time. This is consistent with previous reports (Co_3O_4 [34] and CuO [16]) regarding near-Nernstian pH response. These electrodes were considered viable candidates for disposable pH electrodes, pH microelectrodes and tube and needle-type pH electrodes for novel pH sensors.

4. Conclusions

In the present study, 3d-block metal oxide-coated SUS304 electrodes (MO_x/SUS , $M=Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu$ and Zn) were prepared using the sol-gel dip-coating method in order to develop novel pH sensors. The pH responsivity (pH sensitivity, pH repeatability and initial pH response time) of the MO_x/SUS electrodes was investigated. The following results were obtained.

MO_x/SUS electrodes exhibited a pH sensitivity of 88–100%, a pH repeatability of 0.1–0.6 in pH units and an initial pH response time of approximately 1 sec. The pH sensitivities of the SUS (as-received) and SUS-500 (heated at 500 °C) were 91% and 94%, respectively. Therefore, it appeared that the pH sensitivity of the MO_x/SUS electrode was affected by the underlying materials (SUS substrate and its oxide layer) as well as by the outer MO_x films. All of the MO_x/SUS electrodes exhibited much shorter initial pH response time than a commercial glass electrode (14 sec). In particular, Co_3O_4/SUS and CuO/SUS electrodes were considered candidates for disposable pH electrodes, pH microelectrodes and tube and needle-type pH electrodes for novel pH sensors as a result of their favorable pH sensitivity, pH repeatability and initial pH response time.

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