

lithium ion selectivities in the electrode measurements conducted with the 14-C-4 ionophore 1, which contains an acid side chain, equals or exceeds the lithium ion selectivity of ionophore 3, which contains a neutral chain, depending on the method of measurement and whether or not TOPO was present. This indicates a positive influence of the carboxylic group in the side chain of the 14-C-4 ether. The high lithium ion selectivity of ionophores 1 and 3 with respect to potassium ion in the electrodes is in agreement with the solvent extraction results (11) (lithium  $\gg$  sodium, with no potassium, rubidium, or cesium ion extraction for ionophore 1 and lithium  $>$  sodium  $>$  potassium ion for ionophore 3).

In solvent extraction of metal ions, the carboxylic acid groups of proton-ionizable crown ethers 1 and 2 act as anionic counterions to form a neutral extractable complex, thus avoiding the necessity of adding a separate extractable counterion, such as picrate (12). Normally in solvent membrane electrodes, a neutral crown ether ionophore has been employed and anionic sites are provided by the membrane itself (21). It is interesting to note that in the membrane electrodes the crown ether carboxylic acid 1 exhibits the best potentiometric selectivity, as well as sensitivity, in agreement with the solvent extraction data. This is somewhat surprising since it appears that the nonionized form of 1 is the ionophore in the membrane electrode, whereas the ionized form is the effective metal ion complexing agent in solvent extraction. Apparently even in the nonionized form, the pendant carboxylic acid group in 1 provides an additional coordination site that enhances lithium ion complexation.

Although other membrane ingredients may affect electrode selectivity and sensitivity, these results demonstrate that general trends in solvent extraction selectivity for potentially useful membrane ionophores can be used to predict electrode performance and aid in the design of new synthetic ionophores.

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## Response of Oxide Films on Stainless Steel as a pH Sensor

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**Stable oxide films on two kinds of austenite stainless steel (SUS304 and SUS316) were found to work as a very promising hydrogen ion selective sensor. Both types of oxide film showed a Nernstian response in a pH range of 1-13 within 3 s. The presence of alkali-metal ions, ammonium ion, and other cations was tolerated. The oxide film produced on SUS304 stainless steel was affected seriously by chloride ion, but the film produced on SUS316 stainless steel was found to be little affected by chloride ion.**

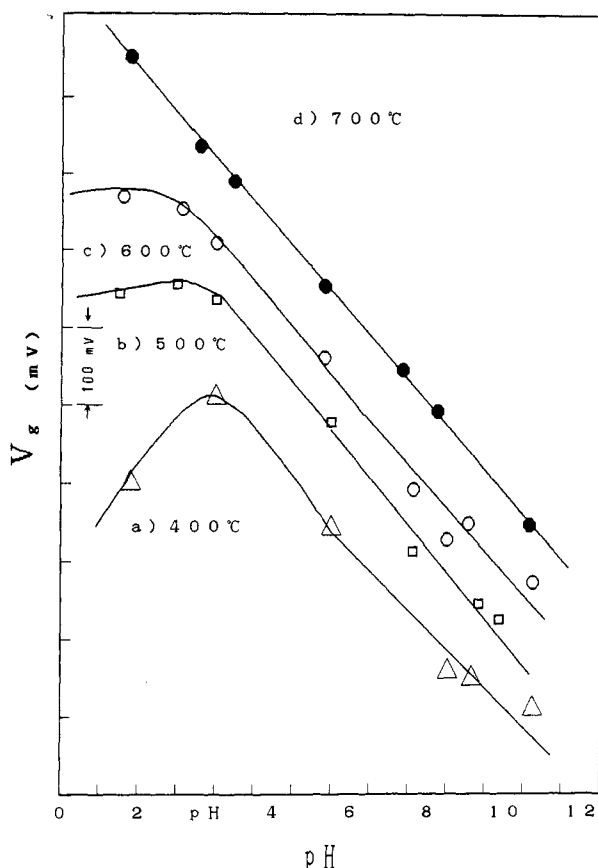
Insoluble and semiconductive metal oxides are sensitive toward hydrogen ion according to the ion exchange mechanism at the active OH sites formed on the metal oxide surface in a solution (1, 2). We reported in the previous paper (3) that magnetite-coated iron wire and molybdenum oxide coated molybdenum wire electrodes showed a near-Nernstian behavior in a pH range from 4 to 11 and in a pH range from 2 to 12, respectively, and that molybdenum oxide film showed a more stable pH response even in solutions containing halide

ions but worse selectivity against cations than magnetite film. It was suggested that any kind of oxide-coated metal could work well as a hydrogen ion sensor if the oxide films were properly prepared. However, the oxide-coated metal electrodes need to be improved so as to be stable over a wider pH range.

Films of mixed metal oxides formed on stainless steel were firm. Consequently, they are expected to show stable response and become a promising hydrogen ion sensor. Since a passive layer on stainless steel was too thin and had too many defects to use as a pH sensor, we made a thicker oxide film on stainless steel by heating and chemical treatment. We selected austenite stainless steel of type SUS304 and type SUS316 because the latter stainless steel contained about 3% Mo in addition to the constituents of SUS304 stainless steel (18% Cr + 8% Ni + Fe). These electrodes are prepared and the pH characteristics are reported.

## EXPERIMENTAL SECTION

Austenite stainless steels (SUS304 and SUS316) were cut, degreased, and oxidized either by heating their sheets in air at 400-700 °C for 1 h in a furnace or by immersing them in a solution

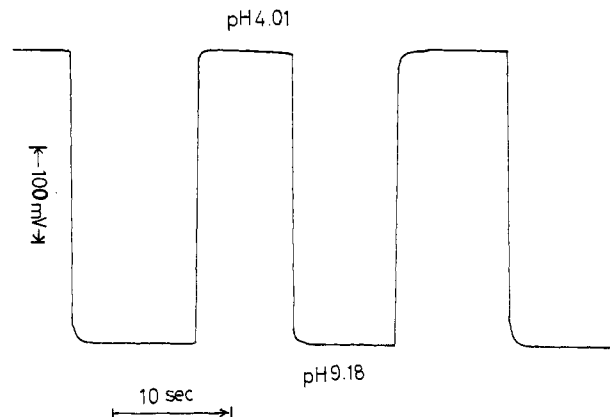


**Figure 1.** pH response of oxide film formed on SUS304 stainless steel heated at (a) 400 °C, (b) 500 °C, (c) 600 °C, and (d) 700 °C for 1 h.

of 2.5 M  $\text{CrO}_3$  and 5 M  $\text{H}_2\text{SO}_4$  at 70 °C for 10–30 min. Several oxide-coated samples prepared by heating in air were further treated in a chromate solution for 1–2 min and washed in water. The oxide-coated stainless steel prepared was connected to the gate of the field effect transistor (FET:2SK241) through a lead wire, and the gate voltage of an oxide-coated stainless steel electrode versus a reference Ag/AgCl electrode was measured with a digital voltmeter (Advantest TR6847 digital multimeter), while the FET worked normally by keeping the source-drain voltage (0.2–3 V) and the current (50–150  $\mu\text{A}$ ) constant using a source follower circuit. The thickness of oxide films on stainless steel was roughly estimated by the weight change of steel and by depth profiling with Auger electron microscopy coupled with argon ion etching, supposing that the oxide films were composed of uniform  $\text{Fe}_2\text{O}_3$ . Several standard solutions (oxalate, phthalate, phosphate, borate, and carbonate buffer solutions) were prepared by adding sulfuric acid or sodium hydroxide solution to adjust the pH of the solutions. The pH values of the standard solutions were simultaneously measured by a glass electrode (Toa Electronics HM-20E pH meter).

## RESULTS AND DISCUSSION

**Oxide Film on SUS304 Stainless Steel.** Sheets of SUS304 stainless steel were heated at 400, 500, 600 and 700 °C for 1 h. The surface became shiny yellow, green, purple, and violet with the elevation of heating temperature. The electric resistance of these films ranged from 0.15 to 0.5  $\Omega/\text{cm}^2$ . The working characteristics of each oxide-coated sheet are shown in Figure 1. The oxide-film electrode prepared by heating at 700 °C showed a Nernstian response in the widest pH range between 1 and 13. Other pH electrodes prepared by dry processing showed the unstable pH response deviated from a Nernstian slope especially under pH 4. That is probably caused either by the presence of microcracks and pinholes, which were generated usually in the thin films by insufficient coverage, or by the change of the oxide surface, which could be incubated by the dissolution of soluble iron

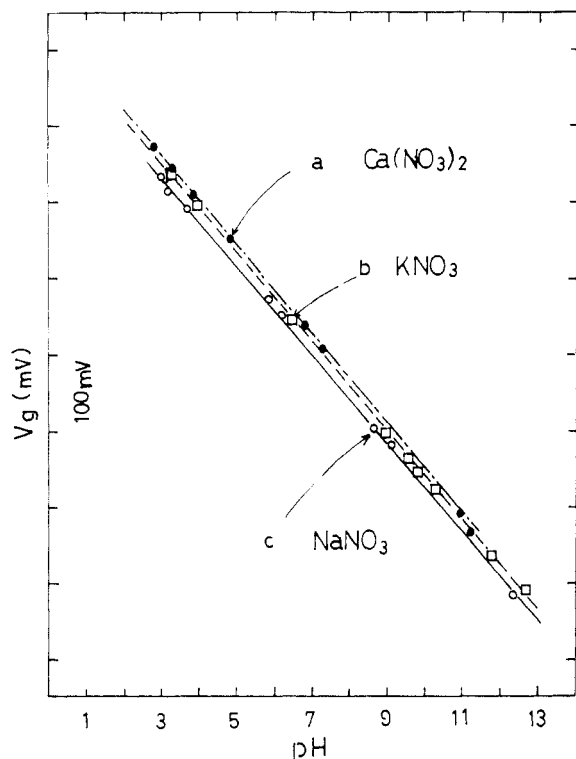


**Figure 2.** pH response time of oxide film on SUS304 stainless steel when the electrode was repeatedly dipped between the solutions of pH 4 and pH 9 while the solutions were stirred.

oxide on the top surface. The presence of the iron oxide on the top surface was supported from Auger electron profiles. Iron of SUS304 stainless steel heated at 400 °C was concentrated on the outermost surface. Chromium content in the outermost surface tended to increase and iron content to decrease with raising oxidation temperature. Boshin et al. (4) measured the similar Auger electron profiles and reported that the pitting susceptibility is strongly influenced by heating due to the formation of defects and chromium deficient zones in the film.

The response of these electrodes was restored to Nernstian by further wet treatment in a chromate solution for 1 min. The oxide films formed on the SUS304 sheet by heating at temperatures higher than 800 °C were black and rough. They were not suitable as pH-sensing films. We further made oxide films of different thickness, about 70 and 100 nm, by treating SUS304 sheets in a chromate solution for 12 and 24 min. The gradients of output voltage versus pH for these electrodes were 58 and 50 mV/pH, respectively. The lower gradient was obtained for a thicker oxide film. Considering that the thicknesses of oxide films prepared by heating at 400 and 700 °C and further treating in a chromate solution for 1 min were 30 and 50 nm, respectively, the most desirable film thickness for pH sensor was estimated to be between about 30 and 70 nm. Since the most desirable thickness of a magnetite-coated iron wire electrode was between 100 and 200 nm (3), the difference of the most desirable thickness between the two was considered to come from the density and uniformity of the oxide films formed on the metal substrate. In order to accomplish faster response, it is important that the uniform film be as thin as possible.

The response time of an oxide-coated stainless steel electrode was about 3 s when the electrode was repeatedly transferred between the solutions of pH 4 and pH 9 while stirring with a magnetic stirrer, as shown in Figure 2. It was much faster than the usual pH glass electrode. An oxide-coated stainless steel electrode was dipped in various 0.1 M solutions of alkali-metal ions ( $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$ ,  $\text{Cs}^+$ ), ammonium ion, sulfate ion, and nitrate ion in order to survey the hydrogen ion selectivity of the electrode. It was found that the coexistence of these ions could be tolerated over a wide pH range between 1 and 13. The working characteristics of the oxide-coated stainless steel pH sensor in 1 M solutions of  $\text{Ca}(\text{NO}_3)_2$ ,  $\text{KNO}_3$ , and  $\text{NaNO}_3$  are shown in Figure 3. Although the slope of the output voltage was slightly shifted parallel by at most about 20 mV, the gradient of the output voltage versus pH remained unchanged. The shift observed in Figure 3 was considered to be caused more by drift of output voltage due to the difference of time when pH measurements were carried out in each solution than by ionic strength in

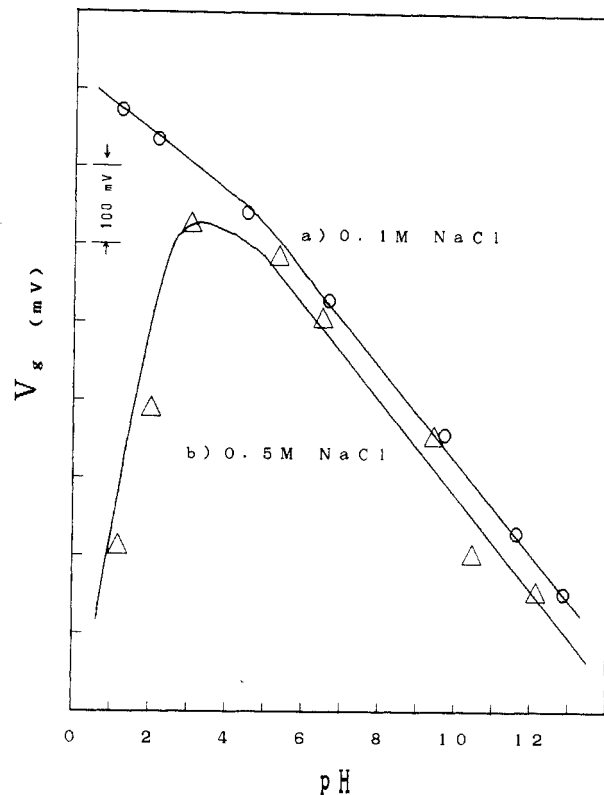


**Figure 3.** Effect of coexisting ions on the pH response of oxide film on SUS304 stainless steel in (a) 1 M  $\text{CaSO}_4$ , (b) 1 M  $\text{NaNO}_3$ , and (c) 1 M  $\text{KNO}_3$  solutions.

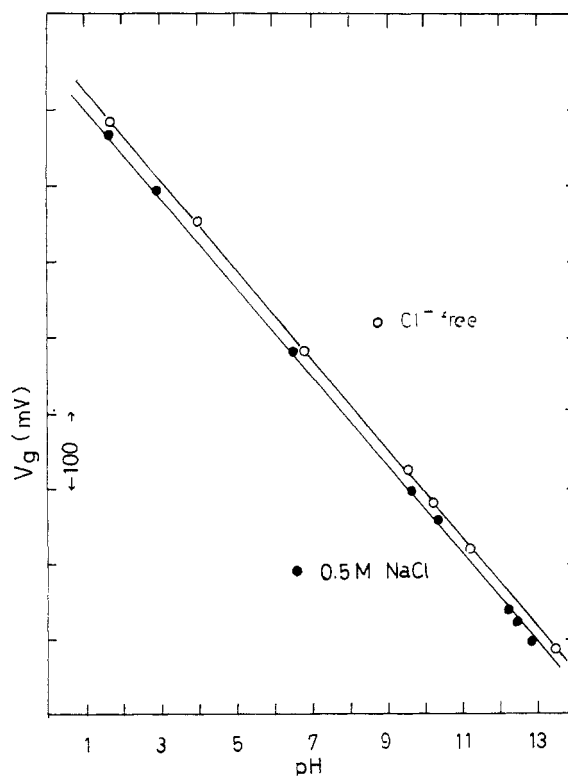
solutions. The initial drifts were about 10 mV/3 h, 20 mV/3 h, 30 mV/3 h, and 45 mV/3 h in a solution of pH 1.68, 4.0, 6.88, and 12.2, respectively, and then a long-term drift of about 20 mV/day was recognized. The drift was considered to occur due to the little variation of the surface condition, which could affect the change of fixed charge plane of oxide surface and the charge distribution of dipole layer formed at the interface between oxide surface and electrolyte.

When the electrode was immersed in 0.1 and 0.5 M NaCl solutions, the response toward pH became unstable and the output voltage decreased remarkably at pH value less than 4, as shown in Figure 4. Chloride ion interfered in the pH measurement in the acid solution seriously probably due to the chemical dissolution reaction of metal oxide by hydrochloric acid.

**Oxide Film on SUS316 Stainless Steel.** The oxide films, prepared on SUS316 sheets by heating in dry air at 600 and 800 °C for 1 h and in wet air at 400 °C for 2 and 4 h, did not show stable response to hydrogen ion. SUS316 stainless steel was immersed in a solution of 2.5 M  $\text{CrO}_3$  and 5 M  $\text{H}_2\text{SO}_4$  at 70 °C for 10–30 min. The oxide film thus formed on SUS316 gave basically the same pH response as the oxide film on SUS304, as far as the measurable pH range and the response time were concerned. The most important difference between the oxide films produced on SUS304 and SUS316 was the effect of chloride ion. The film formed on SUS316 tolerated the presence of chloride ion as shown in Figure 5. The film on SUS316 is more useful as a pH sensing film than the film on SUS304. It was observed by Auger electron spectrometry and an electron probe microanalyzer that the concentration of chromium and molybdenum increased and the concentration of iron and nickel decreased in the outermost oxide of SUS316 stainless steel. Since the oxide film on SUS316 contained molybdenum oxide in addition to the composition of the oxide film on SUS304, molybdenum oxide was considered to play an important role in the prevention of attack by chloride ion. Since surface oxide on stainless steel consisted of chromium-rich oxide layers, the active OH sites of chro-



**Figure 4.** pH response of oxide film on SUS304 stainless steel in (a) 0.1 M and (b) 0.5 M NaCl solutions.



**Figure 5.** pH response of oxide film on SUS316 stainless steel in the various pH solutions (●) of 0.5 M chloride ion and (○) free from chloride ion.

mium oxide could react mainly with the species of the electrolyte, and molybdenum oxide was considered to contribute to the intensity of minus charge at the active sites so as to prevent incorporation of chloride ion into the film.

The addition of molybdenum to metals is known to improve remarkably the resistance to corrosion. This is also supported in the present work of oxide films on stainless steels. Many

researchers have considered that molybdenum oxide contributes to a formation of uniform film with less defects (5), to a formation of amorphous film (6), etc. Nevertheless, it still is left unclear whether or not molybdenum influences the film characteristics to the response of hydrogen ion and the attack of chloride ion in an acid solution at present. In the case of the molybdenum oxide film electrode (3), it had resistance against the chloride ion present in a solution of a pH range between 3 and 11 but showed a Nernstian response in the narrower pH range and a worse selectivity versus pH than that of oxide film formed on stainless steel. Selective coefficient of potassium ion was in level of  $10^{-3}$  for a molybdenum oxide electrode but below the measurable level for an oxide-coated SUS316 electrode. These results suggest that a composite metal oxide film is superior to a monometal oxide film as a pH-sensing electrode.

The initial drift after the immersion in solutions was about  $-60$  mV/2 h at the pH value of 1.68, and about  $20$  mV/2 h at a pH value of 4.0. The response became stable after about 3 h, and a slight drift at the rate of about  $1$  mV/h was observed in each solution. Even when pH measurement was carried out just after dipping a dry electrode, a Nernstian slope could also be obtained at the moment though the response drifted to some extent. The output voltage kept constant within the deviation of at most  $30$  mV with the lapse of time.

In a solution of pH 2.2 containing  $0.5$  M NaCl, the gate voltage decreased suddenly by about  $10$  or  $20$  mV once every 2-4 hours but recovered in about 10-20 min. After 2 days the gradient decreased to about  $30$  mV/pH. Such a phenomenon was not observed in  $0.5$  M NaCl solutions with pH values higher than 3.5. Although pit incubation or nucleation (5) might be originated by the attack of chloride ion, the pit growth was prevented in the oxide film on stainless steel in the high pH solutions. If the hydrogen ion concentration were

high, the active sites could produce a number of positive sites by the adsorption of  $H_3O^+$ . The change of the surface charge would permit the approach of chloride ions to get into the oxide film.

Concerning the long-term stability of the response, the electrode will work well for more than a month if the electrode is not dipped in a solution of NaCl at a pH value less than 3.5.

## CONCLUSION

The oxide films on SUS316 were found to be superior to the oxide films on SUS304 from the view point of suppression of the interference caused by chloride ion in solutions. Calibration of pH needs to be carried out at every measurement as slow drift cannot be controlled at present. The calibration can be easily carried out by adjusting the applied voltage or current between the source and the drain of FET by using only one standard solution.

As any shape of electrode can be fabricated easily depending on the purpose of the pH sensor, the oxide-coated stainless steel electrode will be useful for various types of pH measurements. Because the sensing film is separated from the FET and can be fabricated very easily, metal oxide coated stainless steel sheets are disposable.

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# Investigation and Elimination of Chloride Interference on Thallium in Graphite Furnace Atomic Absorption Spectrometry

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Chloride interferences on thallium are in part caused by volatilization of thallium chloride in the pyrolysis stage and in part by formation of TlCl in the gas phase during the atomization stage. The palladium modifier is not as effective for thallium as it is for other elements. Its stabilizing power can be improved substantially when the modifier is pyrolyzed at  $1000^\circ\text{C}$  before the sample is pipetted. Use of hydrogen purge gas has a similar effect on the stabilizing power of palladium. It was found necessary to apply both these measures, pyrolysis of the modifier prior to the addition of the sample and use of hydrogen, for interference-free determination of thallium in samples with high chloride content such as seawater and urine. A detection limit ( $3\sigma$ ) of  $2\text{ }\mu\text{g L}^{-1}$  was obtained for thallium in both sample types with  $10\text{-}\mu\text{L}$  sample volumes, and the characteristic mass was  $19\text{ }\mu\text{g}$ .

Thallium is an element of substantial toxicity and is therefore of considerable analytical interest particularly in biological and environmental samples. Graphite furnace atomic absorption spectrometry (GF-AAS) provides the required sensitivity and selectivity and is an important tool for determining thallium at low concentrations. However, there appear to be tenacious interferences in the determination of thallium, particularly in matrices containing high chloride concentration. Many analysts therefore prefer complexation and extraction of the analyte prior to its determination, as is summarized in a recent review article on this element (1).

In this work we wanted to investigate to what extent interferences in the determination of thallium, particularly due to chloride, could be overcome when up-to-date equipment and techniques were used. This included for example the use of the stabilized temperature platform furnace (STPF) concept (2) and Zeeman-effect background correction (3, 4). Slavin and co-workers, have shown in several publications that atomization from a L'vov platform substantially reduced the

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