"METOX pH SENSOR" AS pH MEASURING ELECTRODE

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Abstract In this paper we show that the electrode by d.c. reactive sputtering of iridium oxide on the solid substrates have utility for pH sensing. We named this electrode "METOX pH Sensor" in order to distinguish from Glass Electrode.

"METOX pH Sensor" had linear response over a range of 0 to 14 and Nernstian slope 59.15mV/pH. For long-term stability in aqueous solutions, the drift of potential was less than 8 mV over 1000 hrs in pH6.86 buffer solution. Interferences of oxidizing and reducing substances were less than a few millivolts.

Key words pH measurement; pH sensor; iridium oxide electrode

Introduction

The pH is one of the most important parameters for characterizing the chemical properties of aqueous solutions. In the pH measurements of aqueous solutions, so far the glass electrode is the most commonly used as pH sensor. But it has some problems which are not stable for physical and chemical attack, and too hard to miniaturize.

Iridium oxide films are particularly the attractive candidates for pH sensors in near future because of (i) the stability in aqueous solutions over a wide range of temperature and pressure^{1,2}, and low rate of dissolution even in corrosive fluids²; (ii) the low impedance and (iii) the fast response. The pH sensitive of iridium oxide films prepared by reactive sputtering have the following additional advantages over the other film preparations¹⁻⁵; (iv) manufacturing process of electrodes is simple; (v) only a direct deposition technique offers sufficient processing flexibility to be compatible with multiple probe micro-electrode fabrication; (vi) in particular it is not necessary to use iridium substrates.

So, we developed "METOX pH sensor", which is made of Iridium Oxide

Experimental

Iridium oxide films were deposited by d.c. reactive sputtering in a pure oxygen plasma. The substrates (5mm × 10mm sapphire sheet) were mechanically polished, and rinsed in deionized water. The substrates were placed on the water cooled mount and the sputter chamber evacuated to its base pressure of 6×10^{-5} Pa. The iridium target (99.99% purity, 7cm diameter) was pre-sputtered in UHP

oxygen at 8 Pa for a few minutes. The sputter deposition was in 3 Pa oxygen at a power density of 0.5 W cm^{-2} for three hours. The substrate temperature was kept less than 40°C during operation. The resulting films were metallic dark blue and approximately 1000 Å thickness.

Leadwire was connected with electrically conductive epoxy adhesive to the edge of iridium oxide film and further its portion was insulated with epoxy resin from aqueous solution.

The potential versus pH was measured in the solution which pH was adjusted by analytic reagent grade HCl and NaOH. The long-term stability of "METOX pH Sensor" was measured in buffer solution of pH 6.86.

Interferences and selectivity were investigated in a series of experiments, where one of the following compounds was added to the above-mentioned buffer: $\text{K}_3\text{Fe}(\text{CN})_6$, $\text{K}_4\text{Fe}(\text{CN})_6$, $\text{C}_6\text{H}_8\text{O}_6$ (L-ascorbic acid). All experiments were carried out at 25.0°C , unless otherwise noted.

Results and Discussion

We investigated the relationships between sputtering conditions and pH response. We made iridium oxide film by very low rate sputter deposition rate (5Å/min.). The structure was made clear by X-ray pattern and XPS measurements. The X-ray pattern showed only amorphous and the results of XPS measurements showed form of IrO_2 .

TABLE 1. Characteristics of METOX pH Sensor (25°C)

METOX pH Sensor	
pH Range	0 ~ 14
Sensitivity (mV/pH)	59.15
Response Time	1 sec.
Long-term stability	8×10^{-3} (mV/h) (1.3×10^{-4} pH/h)

TABLE 2. Interferences of oxidizing and reducing substances (25°C)

Substance	Concentration mol/l	Stability mV/h (pH/h)	pH Range
$\text{Fe}(\text{CN})_6^{3-}$	1×10^{-3}	0.02 (3.4×10^{-4})	0 ~ 14
	1×10^{-2}	0.04 (6.7×10^{-4})	0 ~ 10
$\text{Fe}(\text{CN})_6^{4-}$	1×10^{-3}	0.04 (6.7×10^{-4})	0 ~ 14
	1×10^{-2}	0.08 (1.3×10^{-3})	6 ~ 14
Ascorbic Acid	1×10^{-3}	0.04 (6.7×10^{-4})	0 ~ 14
	1×10^{-2}	0.08 (1.3×10^{-3})	2 ~ 14

Stability: It was measured in buffer solution containing oxidizing or reducing substances.

pH Range: The entire indicates pH range at which "METOX pH Sensor" show reproducible response in the presence of the interfering substances.

Fig.1 Potential-pH response of "METOX pH Sensor"(25°C)

Fig.2 Long-term stability of "METOX pH Sensor" in pH 6.86 buffer solution at 25°C

The results of this investigation were summarized in TABLE 1. Figure 1. showed a typical relationship between potential and pH response of METOX pH Sensor. These results were obtained by pH measurement of the solutions which were prepared by dropwise addition of hydrochloric acid solution or sodium hydroxide solution. Potential were recorded approximately 1 min. after addition of acid or alkali.

The potential varied linearly with the pH range 0-14 and the slope was a Nernstian sensitivity of 59.15 mV/pH ; hysteresis was not observed. It is possible to conclude that "METOX pH Sensor" did not show any error of acid or alkali.

For the long term stability, "METOX pH Sensor" had very stable in aqueous solutions. For example, Figure 2 showed the drift of electrode potential in pH 6.86 buffer solution, which was a less than 10 mV over 10000 hrs of operation (TABLE 1.).

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$$E = E_0 + 2.303RT/F \log a$$

The potential E of as-prepared electrode had theoretical Nernstian form, $2.303RT/F \log [a]$ is 59.16 mV at 25° C. It is said that the slope of the response and the stability of this electrode depended on the thickness of the oxide film, the iridium oxide surface state, the composition of the oxide layer, and the crystallized conditions. It can be seen from our experiments, that is the relationships between sputtering conditions and pH response, that the controls of the crystallized conditions and the composition of the oxide layer are important to the pH response and stability.

In practical applications, the selectivity is one of the most important characteristics of electrode^{1,3,10}. The interferences of oxidizing and reducing substances to "METOX pH Sensor" were summarized in TABLE 2. There were a little shift in E(mV) versus Time(hrs). The potential of "METOX pH Sensor" gradually decreased with the function of reducing substances and increased with the function of oxidizing substances. For example, the degree of shift was less than 0.04 mV/hrs at $[\text{redox}] = 1 \times 10^{-3} \text{ M}$ at 25°C. Table 2 indicated the range of pH at which the electrode showed reproducible responses under the presense of the interfering substances. This result showed that "METOX pH Sensor" had the sufficient selectivity for ordinary applications.

Conclusion

"METOX pH Sensor" can be used for the measurement of pH in many cases. More work is needed to elucidate the working mechanism of this electrode.

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