pH electrode based on ALD deposited iridium oxide

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Abstract

We have made planar pH electrodes that use iridium oxide (IrOx) fabricated by atomic layer deposition (ALD) as the pH sensitive layer. As far as we know, ALD has not been reported earlier as the method of producing IrOx layer on pH electrodes. The structure built on glass substrate consists of 300 nm thick titanium electrodes coated with 110 nm IrOx layer. When measured against a commercial Ag/AgCl reference electrode, we were able to observe a linear and super-Nernstian pH response over the tested range from pH 4 to pH 10. The average sensitivity of three electrodes was \(-67\) mV/pH at \(22^\circ\)C. After 30 s stabilization time the total drift during the next 90 s remained mainly below 1 mV. The 90 \% response time was determined to be less than 3 s.

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Keywords: pH electrode; ALD; iridium oxide

1. Introduction

For measuring pH the most common choices are glass electrodes, optical fluorescence, ISFETs, and metal oxide electrodes. If one targets an electrically measurable, micro sized, planar, and easy to fabricate pH electrode, an electrode based on proper metal oxide is the most obvious choice. Among the metal oxides, iridium oxide (IrOx) is the most often used choice for pH sensing. Over the years several groups have reported various fabrication methods like electrochemical growth [1], electrodeposition [2], sputtering [3], and thermal preparation [4] for pH electrodes having iridium oxide as the pH sensitive element. As far as we know, atomic layer deposition (ALD) has not been reported earlier as the method of producing IrOx layer on pH electrodes. Compared with many of those other methods, ALD is much more straightforward and unlike in sputtering there is no need to bind capital on source material. As ALD deposits the IrOx film layer by layer, it is possible to control the thickness exactly, which is not necessarily the case with the other methods. Our original motivation for developing stable miniature pH electrodes is the need to measure pH changes in cell culturing environment.

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doi:10.1016/j.proeng.2010.09.168
2. Materials and methods

Our electrodes (Fig. 1 and Fig. 2) were fabricated so that at first 300 nm layer of titanium was e-beam evaporated on a 25 mm x 25 mm x 0.9 mm glass slide and after that the electrode pattern was formed there lithographically. 500 nm layer of Si₃N₄ was PECVD deposited as insulator layer and openings for electrodes (four round ones of 1.4 mm diameter and one 1.8 mm x 9.8 mm square) and contact pads were dry etched with SF₆ and O₂. IrOx was ALD deposited from Ir(acac)₃ and ozone at 185°C in a process of 3000 cycles of 2 s pulses and purges [5]. Based on EDX (energy-dispersive x-ray spectroscopy) measurements, that process led to the IrOx layer thickness of about 110 nm. The fabrication process was concluded by the lift-off of photoresist used as a deposition mask.

pH measurements were started by measuring open circuit voltage against a commercial Ag/AgCl reference electrode (VWR Symphony) at 22°C in commercial buffer solutions having pH from 4 to 10. The voltage readings were recorded after 30 s stabilization time and again 90 s from that. To determine the 90 % response time, a step response from pH 9.9 to pH 7.1 was measured. The step was generated by adding HCl in the initial solution. Finally, we recorded dynamic step response from pH 3.0 to pH 11.1 and back to pH 3.0 in steps of about 1 pH. In each step one minute was reserved for adjusting the pH of the liquid by adding KOH or HCl and after that the pH was let to be constant for five minutes. Before, after, and between all the measurements, the electrodes were stored in normal room atmosphere.

3. Results and discussion

Fig. 3 shows the measured open circuit voltage against a commercial Ag/AgCl reference electrode as a function of the pH of the buffer solution. The curves indicate a very linear pH response and as the average slope of the linear fits, i.e. the sensitivity, is about 67 mV/pH, the response can be considered super-Nernstian. Also drift was evaluated while those measurements. Usually, the drift during 90 s after 30 s stabilization time remained below 1 mV, which can be considered rather low.

The step response curve for a step from pH 9.9 to pH 7.1 is shown in Fig. 4. As presented with the other results in Table 1, the average 90 % response time was determined to be 2.9 s. However, because the pH step was generated by adding HCl in the solution, the response time includes also the time needed to get the acid totally mixed with the initial solution, and thus the actual response speed can be considered even faster.
Table 1. Specifications of ALD IrOx based pH electrodes: Number of ALD cycles, IrOx layer thickness, usual drift in 90 s after 30 s stabilization time, average sensitivity, and average 90 % response time of three pH electrodes.

| Number of ALD cycles | IrOx thickness (nm) | Sensitivity (mV/pH) | Drift in 90 s (s) | 90 % response time (s) |
|----------------------|---------------------|---------------------|-------------------|------------------------|
| 3000                 | 110                 | -67                 | < 1               | < 2.9                  |

The recorded dynamic step response from pH 3.0 to pH 11.1 and back to pH 3.0 in steps of about 1 pH is presented in Fig. 5. Even if some hysteresis can be observed, the voltage still returns to the initial level when returned to pH 3.0. The reason not to study the full pH range from 1 to 14 was just to play safe with the limited amount of electrodes fabricated and also in our intended primary application field, cell culturing, measuring extreme pH values is not required. In any case, we expect there to be no reason why both the sensitivity and dynamic step response results could not be extended over the full pH range.

Our preliminary measurements with other IrOx layer thicknesses indicate that not only the pH sensitivity, but also response time increase as a function of thickness. It will then depend on application how to optimize the thickness in each case. Another issue, possibly having effect on performance, is the conductor material below the IrOx layer. The now used conductor, titanium, is a cheap, durable, highly biocompatible, and easy to pattern material that has good adhesion properties both to glass substrate and IrOx. But a few nm thick native oxide on top, however, may affect the device properties and therefore evaluation of other conductor materials in the future is necessary.

One issue totally neglected in this study was paying special attention on how to store the electrodes before, after, and between the measurements. Perhaps storing the electrodes in certain buffer solution or water instead of dry storage in normal room atmosphere might affect the stability as well as the total life time of the electrodes, both issues not yet evaluated.

In certain cell culturing applications one main challenge for the pH measurements, in addition to biocompatibility, is often the limited space available for the pH and reference electrodes. That and also general interest leads us to study in the future how small electrode area we can go to in order to retain both the pH sensitivity and response time at reasonable level. The ultimate goal would be integrating both pH electrode and reference electrode as a micro sized sensor chip.

![Fig. 3. pH response and linear fits of three electrodes](image-url)
4. Conclusions

Planar pH electrodes based on ALD deposited iridium oxide have linear and super-Nernstian pH response. The observed average sensitivity of three electrodes was -67 mV/pH at 22°C over the tested range from pH 4 to pH 10 when measured against a commercial Ag/AgCl reference electrode. The 90 % response time was determined to be less than 3 s. IrOx coated electrodes are also rather stable, the total drift in 90 s remaining mainly below 1 mV after 30 s stabilization time. The achieved results encourage us to continue developing the pH electrodes further both for general use as well as for our initial application field of cell culturing.

Acknowledgement

This work was supported by the Academy of Finland (decision number 123359), CHEMSEM graduate school and Biosensing Competence Centre (BCC).

References

[1] Olthuis W, Robben MAM, Bergveld P, Bos M, van der Linden WE. pH sensor properties of electrochemically grown iridium oxide. Sens Actuators B Chem 1990;2: 247-256.
[2] Marzouk SAM. Improved Electrodeposited Iridium Oxide pH Sensor Fabricated on Etched Titanium Substrates. Anal Chem 2003;75: 1258-1266.
[3] Kreider KG, Tarlov MJ, Cline JP. Sputtered thin-film pH electrodes of platinum, palladium, ruthenium, and iridium oxides. Sens Actuators B Chem 1995;28: 167-172.
[4] Yao S, Wang M, Madou M. A pH Electrode Based on Melt-Oxidized Iridium Oxide. J Electrochem Soc 2001;148: H29-H36.
[5] Hämäläinen J, Kernell M, Munnik F, Kreissig U, Ritala M, Leskelä M. Atomic Layer Deposition of Iridium Oxide Thin Films from Ir(acac)₃ and Ozone. Chem Mater 2008;20: 2903-2907.