Metal oxide sensors for long term pH monitoring

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Introduction

The determination of pH, a measure of concentration of hydrogen ions in a solution, is an important task in analytical chemistry since various biological and chemical reaction mechanisms are pH dependent. While the conventional glass type electrodes are widely used for their high accuracy; they are not amenable to miniaturization, and suffer from sluggish response [1], [2], [3]. Various solid-state metal oxide pH sensing electrodes, chiefly iridium oxide and ruthenium oxide (RuOx), have been investigated as an alternate. RuOx exhibits several unique advantages over other metal oxides such as thermal stability, excellent corrosion resistance, low hysteresis, low cost and high sensitivity [4]. In this work, we developed and investigated the long-term performance of the RuOx films on platinum electrode. The sensors exhibited near-Nernstian response at 55 mV/pH and long-term stability of over 4 weeks.

Sensor fabrication

The sensors were fabricated using standard photolithography and lift off processes (See Fig 1A). The diced glass chip with ruthenium oxide pH sensor electrode is 2.3 x 4.3 mm and has connection pads and tracks made of platinum. A dielectric material is used for passivation of sensor tracks. The fabricated sensors were hydrated in phosphate buffer saline (PBS) at pH 7.4 for 6 days before measurement. All the potentials reported were measured against a commercial double junction reference electrode (RE) (Sigma Aldrich, UK) The sensors were calibrated in commercial buffers (Reagecon, Ireland). The data was acquired using high input impedance (1130 pH adapter, Phidget, Canada) and an analogue-to-digital converter (Phidget interface kit 8/8/8, Phidget, Canada).

Results

Fig 2 shows the OCP (open circuit potential) of the developed sensors to the pH change. The transient response in Fig 2(A) shows a short equilibration time, thus demonstrating a fast response. The sensors showed a stable sensitivity of ~ 55 mV/pH over 60 days period. Fig 3 shows the low drift in the potential for two of the sensors, over 60 days. The gap in the data is due to the data logging in the measurement system.

Conclusions

A miniaturized pH sensor has been fabricated using ruthenium oxide as the pH sensitive electrode. The sensor developed shows near-Nernstian response and a low drift over 4 weeks. We anticipate the developed sensors with an integrated reference electrode can be used for sensing pH change in various biological and chemical environments.

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Figure 1: (A) Schematic of the fabrication flow for the pH sensors. (B) Microscope image of a RuOx pH sensor. Scale bar 500 µm.

Figure 2: (A) Potential response of RuOx sensors to different pH buffers (pH 6, 7 and 9). (B) Potential vs measured pH for 3 RuOx sensors, showing sensitivity of ~ 55 mV/pH. (C) Drift in the sensitivity of the sensors over 5 weeks time period.

Figure 3: Long term OCP of two of the fabricated RuOx sensors in PBS pH 7.4 against a commercial reference electrode.

References