Effect of ordered mesoporous carbon contact layer on the sensing performance of sputtered RuO_2 thin film pH sensor

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ABSTRACT

The effect of contact layer on the pH sensing performance of a sputtered RuO_2 thin film pH sensor is investigated. The response of pH sensors employing RuO_2 thin film electrodes on screen-printed Pt, carbon and ordered mesoporous carbon (OMC) contact layers are measured over a pH range from 4 to 10. Working electrodes with OMC contact layer are found to have Nernstian pH sensitivity (−58.4 mV/pH), low short-term drift rate (5.0 mV/h), low hysteresis values (1.13 mV) and fast reaction times (30 s), after only 1 h of conditioning. A pH sensor constructed with OMC carbon contact layer displays improved sensing performance compared to Pt and carbon-based counterparts, making this electrode more attractive for applications requiring highly-accurate pH sensing with reduced conditioning time.

1. Introduction

Radio frequency magnetron sputtering (RFMS) is a convenient technique for the deposition of metal oxides, producing uniform thin films with well controlled properties and thickness [1,2]. RFMS deposition of thin metal oxide films under controlled parameters has been demonstrated for the production of solid state pH sensors with excellent performance [1–3]. In particular, sputter deposited RuO_2 has been used in the construction of pH sensors with excellent performance, due to its Nernstian pH sensitivity, low hysteresis widths and excellent corrosion resistance [1,2,4,5]. To manufacture a pH sensitive working electrode the metal oxide layer is typically deposited onto an electrical contact, as illustrated in Fig. 1. Previous work on membrane based ion sensitive electrodes (ISEs) have shown that the choice of contact material is critical for determining the sensor's performance [6,7]. However, the effect of contact layer material on the performance of solid state potentiometric metal oxide based pH sensors has never been comprehensively investigated.

Sputter deposition of thin metal oxide films onto precious-metal electrodes (e.g., Pt and Au) has been demonstrated for the construction of pH sensors [3,8]. However, these precious metals are expensive. Carbon electrodes are an excellent alternative to their precious-metal counterparts, since they offer two key properties needed for developing viable pH sensors, namely, cost effectiveness and chemical inertness [9]. Particularly, Ordered Mesoporous Carbon (OMC) has an extremely well ordered structure with pores between 2 and 50 nm in diameter

[10]. Due to its unique structure, OMC exhibits high specific pore volume and large surface area resulting in high double layer capacitance and a high number of favourable sites for electron transfer [10,11]. Due to these properties, along with its chemical inertness and high thermal stability, OMC is an attractive material for the development of viable electrochemical sensors [11,12].

Specifically, OMC electrodes have been used in the construction of ISEs [7,13] and amperometric biosensors [11,14]. Owing to their high double layer capacitance, ISE electrodes employing an OMC solid contact layer have excellent ion-to-electron transduction and good potential stability [7,13]. Amperometric biosensors constructed using OMC have demonstrated significantly higher sensitivity in comparison with conventional biosensors [11,14]. In this paper, the pH sensing performances of sensing electrodes, based on Pt, carbon and OMC contact layers in conjunction with thin RuO_2 films, are investigated. Experimental results show that the OMC-based sensing electrode exhibits the best performance, attaining a Nernstian pH sensitivity of 58.4 mV/pH, low short term drift rate of 5.0 mV/h, hysteresis values as low as 1.13 mV and a 30 s reaction time. These properties make OMC-based RuO_2 electrodes a more suitable candidate for pH sensing applications requiring high accuracy and relatively-short conditioning time.

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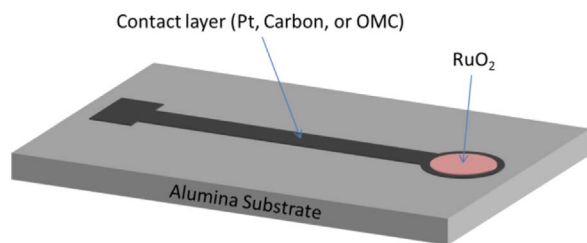
Fig. 1. Diagram of a solid-state potentiometric working electrode, showing a RuO$_2$ thin film, an intermediate contact layer (made of Pt, carbon or OMC) on an alumina substrate.

2. Experimental details

2.1. Electrode fabrication

Thin-film RuO$_2$ pH working electrodes were fabricated using the method reported in [15,16]. A 300 nm thin-film of amorphous RuO$_2$ was deposited at room temperature using R.F. magnetron sputtering in conjunction with shadow masking onto platinum (Pt), carbon, and OMC contact layers (of 4 mm diameter), which were screen-printed on alumina substrates purchased from Dropsens (DRP-550, DRP-110 and DRP-110OMC). The thickness of the contact layers were 8 ± 3 μm, 15 ± 4 μm and 15 ± 4 μm for Pt, carbon and OMC, respectively. RuO$_2$ was deposited from an RuO$_2$ target (99.95% purity) using an 8:2 Ar:O$_2$ process gas ratio at 1 mTorr pressure, with R.F. sputter power of 100 W.

2.2. Electrode characterization

An Agilent 34410A high performance digital multimeter was used for real-time potential recording between the RuO$_2$ sensing electrodes, and a commercial Ag|AgCl|KCl double junction reference electrode (purchased from Sigma Aldrich). All measurements were made at 20 s intervals; except for the reaction time, where 0.5 s intervals were used. An in-house developed unity-gain impedance-matching buffer amplifier was used to improve the signal-to-noise-ratio of the sensor. Electrodes were conditioned in pH 7 buffer for 1 h prior to use and all measurements were made at 22 °C with continuous magnetic stirring.

Electrode performance was evaluated by cycling the pH solution at the electrode from 7-4-7-10-7 three times, at 3 min intervals, using commercial buffer solutions of pH 4, 7 and 10 (Rowe Scientific, Australia). Sensors were cleaned with a blast of air between measurements. Data points were averaged and used to calculate sensitivity, E° and hysteresis of the sensors; with error bars representing the 95% confidence interval. The short term drift rate was determined over the test period for measurements made in pH 7 buffer; where the line of best fit for this data represents the drift rate and the line of worst fit was used to calculate the errors for this measurement. The reaction time, defined as the time taken to reach within 1 mV of the stable potential [17], was determined for each sensor by equilibrating the RuO$_2$ working electrode in pH 4 or 10 for 3 min, then recording the potential change over 60 s, after exposing the sensor to pH 10 and 4, respectively.

Cyclic voltammetry was performed using a Modern Water PDV6000plus voltammetric instrument fitted with an Ag/AgCl refer-

ence electrode and Pt wire auxiliary electrode. Measurements were made in 0.5 M H$_2$SO$_4$ from 0 to 800 mV at sweep rates from 3.0 to 50 mV/s. The current measured at 400 mV for different sweep rates was used to determine the electrode capacitance [18,19].

3. Results and discussion

3.1. Sensitivity and E° value

Dissociative adsorption of H$_2$O at the RuO$_2$ surface (hydration) results in the formation of −OH groups, which can donate or accept a proton, giving the following reversible reaction [20]:

$$Ru^{(IV)}O_2 + e^- + H^+ \leftrightarrow Ru^{(III)}O(OH) \tag{1}$$

where the potential of an electrode is given by a modified version of the Nernst equation:

$$E = E^0 - \frac{RT}{F}ln\frac{a[Ru^{III}]}{a[Ru^{IV}][H^+]} = \left[E^0 - \frac{RT}{F}ln\frac{a[Ru^{III}]}{a[Ru^{IV}]}\right] - \frac{RT}{F}ln[a[H^+]] \tag{2}$$

where E° - standard potential, R – universal gas constant, T – absolute temperature, F – Faraday constant and $a[Ru^{III}]$, $a[Ru^{IV}]$ and $a[H^+]$ – activity of Ru^{III}, Ru^{IV} and H$^+$, respectively [20,21]. Eq. (2) can be simplified to:

$$E = E^* - 58.6pH \tag{3}$$

where E is the measured potential in mV at 22 °C.

As shown in Table 1 and Fig. 2, all electrodes exhibited a response within 0.6 mV/pH of the expected Nernstian sensitivity, and excellent linearity (R^2 values 0.9999 or greater [22]). However, the E° value decreased as the contact layer material was changed from Pt to carbon to OMC (Table 1 and Fig. 2). Eq. (2) suggests that the decrease in E° potential is due to a greater proportion of Ru^{IV} in the RuO$_2$ layer, which is the result of a difference in hydration of the electrodes. However, as stated by Bakker et al. [17], the potential measured between the working and reference electrodes of a potentiometirc sensor is the sum of all the phase boundary potentials in the circuit (e.g. incluidng the wires and electrical connections), of which only one potential is sample dependent (the sensing membrane). This means the lower E° values observed here could also be due to a lower interfacial potential between the different contact materials and RuO$_2$. This was confirmed by the observation that the electrodes equilibrated to different potentials after 48 h in pH 7 buffer (not shown). It should be noted that the shift in E° potential between the electrodes is not significant and would be accounted for during device calibration.

3.2. Stability

According to Hu et al. [13], at steady state equilibrium, a polarizable electrode exhibits the same potential as a galvanostatically charged capacitor, given by the following equation:

$$E = E^0 + i\left(R + \frac{t}{C}\right) \tag{4}$$

where i is the current flowing through the electrode, R and C are the electrode's bulk resistance and low-frequency capacitance respectively, and t is time. Therefore, using Eq. (4), the rate of change of potential with respect to time (i.e., the drift rate) is given by:

Table 1
Summary of sensitivity, E°, R^2, hysteresis, drift rate and reaction time for RuO2 working electrodes with different contact layers.

Contact Layer	Sensitivity (mV/pH)	E° (mV)	R^2	Hysteresis (mV)	Drift Rate (mV/h)	Reaction time (s)
Pt	−58.6 ± 1.8	925 ± 12	1.0000	6.45 ± 3.2	23.4 ± 1.2	21 ± 5
Carbon	−59.2 ± 1.6	800 ± 11	0.9999	5.44 ± 2.7	20.5 ± 1.1	26 ± 5
OMC	−58.4 ± 0.35	670 ± 1.8	0.9999	1.13 ± 0.76	5.0 ± 1.8	29 ± 6