Manufacture and application of RuO_2 solid-state metal-oxide pH sensor to common beverages

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A new reproducible solid-state metal-oxide pH sensor for beverage quality monitoring is developed and characterised. The working electrode of the developed pH sensor is based on the use of laser-etched sputter-deposited RuO_2 on Al_2O_3 substrate, modified with thin layers of sputter-deposited Ta_2O_5 and drop-cast Nafion for minimisation of redox interference. The reference electrode is manufactured by further modifying a working electrode with a porous polyvinyl butyral layer loaded with fumed SiO_2. The developed pH sensor shows excellent performance when applied to a selection of beverage samples, with a measured accuracy within 0.08 pH of a commercial glass pH sensor.
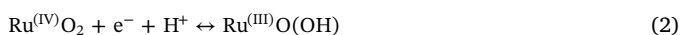
1. Background

The compatibility of solid-state metal-oxide pH sensors with microfabrication techniques makes them more advantageous compared to traditional glass pH sensors, since they can be miniaturised and mass produced [1,2]. In addition such sensors are more cost-effective to produce and more mechanically stable than traditional glass pH sensors [3–5]. Radio frequency magnetron sputtering (RFMS) is one of the most attractive methods for the cost-effective mass production of robust solid-state metal-oxide pH sensors, as it consistently produces films with well controlled thickness and stoichiometry [2,6].

IrO_2 is well known for its excellent pH sensing capabilities [7–9]. However, RuO_2 is a cheaper alternative to IrO_2 and has been shown to have comparable performance [4,10–13]. When hydrated a reversible redox-couple is formed between two oxidisation states, according to the following equilibrium equation:

$$RuO_x(OH)_y + ze^- + zH^+ \leftrightarrow RuO_{x-y}(OH)_{y+z} \qquad (1)$$
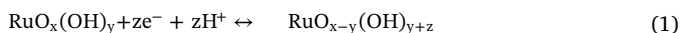
which simplifies to:

$$Ru^{(IV)}O_2 + e^- + H^+ \leftrightarrow Ru^{(III)}O(OH) \qquad (2)$$

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

$$E = E^0 - \frac{RT}{F}\ln\frac{a[Ru^{III}]}{a[Ru^{IV}][H^+]} = \left(E^0 - \frac{RT}{F}\ln\frac{a[Ru^{III}]}{a[Ru^{IV}]}\right) - \frac{RT}{F}\ln(a[H^+]) \qquad (3)$$

where E^0 - 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. When the electrode is at equilibrium, a stable ratio of Ru^{III} to Ru^{IV} is obtained and Eq. (3) simplifies to:

$$E = E^* - 58.6\text{pH} \qquad (4)$$

where E is the measured potential in mV at 22 °C and E^* represents the electrode's potential at a pH of 0 [9,14].

However, metal-oxides are oxidised or reduced by strong redox agents in solution, which results in a shift in the oxide ratio and the E^* value [15]. This limits metal-oxide pH sensors to applications with relatively "simple" sample matrices, such as fresh surface-waters [16]; or applications where high accuracy is not essential, such as acid-reflux [17] or bacteria detection [3,18]. In order to apply metal-oxide pH sensors to more complex sample matrices, electron transfer between the metal-oxide and sample solution needs to be blocked, whilst, maintaining proton conduction to the electrode's surface [19,20].

Prevention of redox-interference for metal oxide pH sensors has partially been achieved by Kinlen et al. [19], who showed that a thermally cured layer of Nafion polymer is able to prevent redox-interference from ferri/ferrocyanide and reduce interference caused by I⁻ and MnO_4^- ions. Nafion has also been used in other works [21,22], however, in these cases, Nafion was not cured and its function was to improve the durability of the metal-oxide by preventing its delamination or dissolution [23–25]. Kuo et al. [26] have reported another approach to eliminate redox interference for a metal-oxide pH sensor. In their work, they placed a thin layer (76 nm) of Ta_2O_5 (a proton-
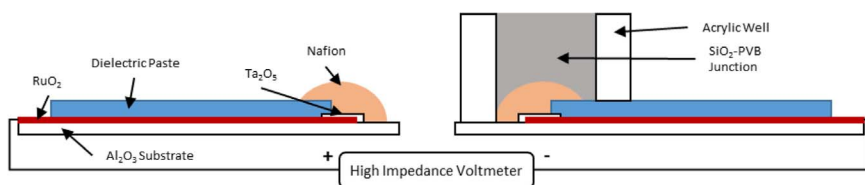
Fig. 1. Schematic showing the construction of the sensor (note that the diagram is not to scale). Working electrode (left) and reference electrode (right).

conducting, electrical-insulator) over a pH sensitive IrO_2 electrode. They demonstrated that this layer blocked interference caused by dissolved oxygen, whilst still allowing pH sensitivity.

A potentiometric pH sensor also requires a reference electrode; in previous work it was shown that modification of a RuO_2 electrode with a porous layer of polyvinyl butyral (PVB) loaded with ground silica functions as a suitable reference electrode, to manufacture an all solid state pH sensor [27]. The purpose of this work is to manufacture a solid-state potentiometric pH sensor employing a Ta_2O_5|Nafion modified RuO_2 working electrode, and a Ta_2O_5|Nafion|PVB-SiO_2-junction modified RuO_2 reference electrode, then, compare the performance of this sensor to a commercial glass pH sensor in some common beverage samples.

2. Method

2.1. Sensor fabrication

Sensor working-electrodes were manufactured by depositing 500 nm of RuO_2 onto a 1 mm thick Al_2O_3 substrate. RuO_2 was deposited using RFMS from an RuO_2 target (99.95% purity) with 100 W sputter power in a 1:9 Ar:O_2 process gas ratio at 4 mTorr (53 Pa) chamber pressure, at room temperature. The electrode working area, conductive track and electrical connection-pad were formed by etching RuO_2 with a Speedy 360 Flex Trotech laser micromachining system (75% power, 8% speed and 4 passes). The working electrode's geometric area was 3.14 cm^2 (2 mm diameter), the actual surface area was not determined, as it was not necessary for device characterisation. The working area was modified with 80 nm of Ta_2O_5, which was deposited using RFMS from a Ta_2O_5 target (99.95% purity) using 200 W sputter power in a 1:9 Ar:O_2 process gas ratio at 4 mTorr (53 Pa) chamber pressure, at room temperature. The electrode working area was then isolated using an insulating Gwent dielectric paste (dried at 120 °C for 20 min). Following electrode isolation, the electrode was modified with Nafion, by drop casting 5 µl of 5% Nafion solution (Sigma) onto the electrode working area, which was cured at 230 °C for 15 min under vacuum (< 10 mTorr), using rapid thermal annealing (RTA). As shown in Fig. 1, left side.

The sensor's reference electrode was manufactured by further modifying a RuO_2 working electrode with an acrylic well filled with PVB-SiO_2 junction material. A well was created around each electrode working area by gluing (Loctite Super Glue-Gel Control) an acrylic ring (5 mm internal diameter, 7 mm outside diameter, 5 mm height) that was made using the laser micromachining system. Once the glue had completely dried, wells were filled with 25 mg of fumed-SiO_2 (Sigma) and topped with a total of 500 µl of PVB solution, in 100 µl aliquots, which were allowed to dry between additions. The PVB solution was prepared by mixing 240 mg of PVB and 50 mg fumed-SiO_2 with 2 mL of anhydrous methanol in a vial, which was homogenized using an ultrasonic bath until uniform (60 min). As shown in Fig. 1, right side.

2.2. Measurements

An Agilent 34410A high performance digital multimeter was used to record potential between the manufactured working and reference electrodes. Potential was recorded for 180 s at 1 s intervals using an NPLC (set to 1) operating in the high-impedance mode. Calculations
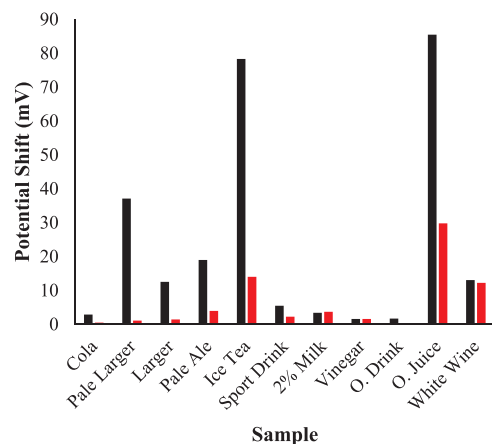

Fig. 2. Potential shift that occurred during 5 min of exposure to various beverages, for an unprotected RuO_2 electrode (black) and a Ta_2O_5|Nafion modified RuO_2 working electrode (red). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

were made by averaging the last 30 data points from each potential recording to produce individual measurements. These measurements were then used to calculate the sensitivity, E^*, hysteresis and drift of the sensor. Hysteresis was calculated using the difference between consecutive measurements at pH 4, whilst electrode drift was calculated using the slope of the line-of-best-fit for the data at pH 4, over the measurement period. Electrode reaction time was defined as the time taken to reach within 3 mV (i.e. 0.05 pH, half the precision of the sensor) of the stable potential. Measurements were made at 22 °C and error-bars represent the 95% confidence interval. Buffer solutions were made by adjusting Britton-Robinson buffer (0.04 M H_3BO_3, 0.04 M CH_3COOH and 0.04 M H_3PO_4) to the desired pH using 0.1 M KOH.

3. Results

3.1. Ta_2O_5 and Nafion protective layers

Unprotected RuO_2 working electrodes manufactured on Al_2O_3 substrates by sputtering and laser etching exhibited excellent performance; i.e. Nernstian sensitivity (58.8 mV/pH), linear response from pH 2–12 ($R^2 > 0.9999$), low hysteresis (1.3 mV), low drift (2.9 mV/h) and acceptable reaction times (< 30 s). Such performance over this wide pH range is useful for many potential applications, however, these electrodes exhibit large shifts in potential when exposed to redox agents. Addition of a Ta_2O_5 layer to the electrode was found to eliminate potential shifts (interference) caused by changes in dissolved oxygen concentration, which is in agreement with results reported by Kuo et al. [26]. However, Ta_2O_5 did not block interference from stronger redox agents (1 mM $KMnO_4$ and ascorbic acid). Interference from stronger redox agents was reduced by Nafion, but not completely eliminated. Thicker layers of Nafion reduce interference more (than thinner layers), however, this was at the cost of greatly increased reaction time in the neutral region, as reported by Kinlen et al. [19]. In addition, Nafion was found to reduce interference from dissolved oxygen, but not eliminate it.

Based on these preliminary experiments (not shown), modification