New operational modes for the Ta₂O₅-based electrolyte conductance cell

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Abstract

Based on the recently presented conductance cell, two specific operational modes are proposed. In the oscillator mode, the conductivity of the electrolyte determines the frequency of an oscillator, experimentally obtaining a shift from 10 to 27 kHz for a KCl concentration range from 0.5 to 100 mM. In the pole mode, an inductor is placed in series with the cell, giving the real electrolyte resistance at the resonance frequency of the circuit, resulting in a linear relation between the log of the output voltage from 4 to 1000 mV as a function of the log of the KCl concentration, ranging from 0.2 to 100 mM.

Introduction

Electrolytic conductance sensors can be used for two different areas: they can either be applied to determine directly the conductance of a solution or they can form the basic transducing element of e.g., a biosensor, where a preferably specific reaction of the analyte can take place with immobilized species in a membrane that is applied on top of the conducting probe [1]. This reaction should be attended with a change in conductivity of the membrane.

Both mentioned fields of application pose specific requirements to the cell: the former needs conductance sensors, capable of measuring in chemically aggressive analytes or withstanding severe chemical or mechanical cleaning and the latter is served with small, planar conductance probes with intricately shaped electrodes.

Recently, a probe for measuring electrolytic conductance has been proposed and realized of which the electrodes are provided with a thin Ta₂O₅-insulating film [2]. This mechanically hard and chemically highly resistant film is applied by IC-compatible processes and photolithographically shaped, allowing small and sophisticated electrode geometries. The specific nature of the Ta₂O₅-solution interface provides the probe with a stable and relatively low oxide-solution impedance that reduces interfering effects from redox processes. Although the conductance cell was shown to operate successfully, the operating frequency had to be chosen

relatively high for proper operation, causing parasitic capacitances to complicate the correct interpretation of the signal.

In this paper, two alternative operational modes are proposed, still using the features of the recently developed conductance probe. Both modes of operation will be discussed and corresponding measurement results will be shown.

Modes of operation

It is shown in the previous paper concerning this subject [2], that due to the low impedance of the Ta₂O₅-solution interface and the non-conducting oxide film, the total conductance cell can be represented by two ideal and constant capacitors, C_{ox} , determined by the oxide layer, and the electrolyte resistance, R_b , connected in series as indicated in Fig. 1. This representation of

Fig. 1. Simplified schematic representation of the conductance cell with capacitive electrodes.

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the conductance cell forms the starting point of the two alternative operational modes.

Oscillator mode

The first mode to be discussed, the oscillator mode, utilizes the specific nature of the Ta_2O_5 film and its interface with the solution, being ideal capacitors as shown in Fig. 1, where the value of R_b is the only variable which can therefore exclusively determine the frequency of an oscillator. From the measured frequency, the electrolytic conductance can be derived.

There is one restriction on the representation of the conductance cell (Fig. 1), which limits the number of possible oscillators and that is the impossibility to contact electrically the point between C_{ox} and R_b . Physically, this spot represents the liquid film immediately adjacent to the oxide layer. Even with this restriction, it is in principle possible to use a classical example of the harmonic oscillators: the Wien-bridge oscillator [3]. The bridge network of this type of oscillator is given in Fig. 2. The upper part of this network could be replaced by the conductance cell that, of course, can be represented by one capacitor of value $1/2C_{ox}$ and resistor R_b . The values of the capacitors and resistors of Fig. 2 must be carefully chosen in order to maintain the demanded phase shift, necessary for oscillation. So, if the electrolyte resistance, represented by $R = R_b$, which is the parameter to be determined, changes, then also one of the other components of Fig. 2 should change its value in order to guarantee oscillation. For this reason, this type of oscillator and with that all harmonic oscillators were abandoned.

A quite different approach is the use of an a-stable multivibrator, which generates a square-wave signal. Using common CMOS inverters, such a multivibrator can be obtained by the circuit design shown in Fig. 3 [4]. Here, R_x and C_x are the essential frequency determining components and R_s is introduced in order to be less dependent on the supply voltage, V_{dd} . For the well-known CMOS binary logic series CD40XX,

Fig. 2. (Left) The bridge network of a Wien-bridge oscillator.

Fig. 3. (Right) The circuit design for an a-stable multivibrator using inverters.

the cycle time T of the square-wave signal can be calculated to be:

$$T = -R_x C_x \left[\ln \frac{V_{tr}}{V_{dd} + V_{tr}} + \ln \frac{V_{dd} - V_{tr}}{2V_{dd} - V_{tr}} \right] \quad (1)$$

where V_{tr} is the transfer voltage, i.e., the voltage where the inverter changes its binary state. If $V_{tr} = 1/2V_{dd}$, then eqn. (1) reduces to $T = 2.2R_x C_x$.

The conductance probe is proposed to replace resistor R_x of Fig. 3. Proper operation can only reasonably be expected if C_x remains the time-determining element and the conductance probe can be represented by the resistor R_b only. For this reason C_x has to be chosen approximately 10 times smaller than $1/2C_{ox}$. The experimental results of this mode of operation will be shown later in this paper.

Pole mode

The second mode of operation, the pole-mode, is also based on the favourable behaviour of the Ta_2O_5 film, resulting in ideal series capacitors. In this mode an inductor is placed in series with the conductance cell of Fig. 1, resulting in an equivalent circuit as shown in Fig. 4. The total impedance of this circuit is:

$$Z(j\omega) = j\omega L + \frac{1}{j\omega C} + R_b = R_b + j \left(\frac{\omega^2 LC - 1}{\omega C} \right) \quad (2)$$

where $C = 1/2C_{ox}$.

At the resonance frequency of the inductor-capacitor part of the circuit, $\omega_{res} = 1/(LC)^{1/2}$, the complex impedances of both elements cancel out, only leaving the electrolyte resistance R_b that determines the measured impedance. One of the possible methods to measure R_b in practice is the application of a constant-current source as shown in Fig. 5.

As the frequency of the current source is adjusted to the mentioned resonance frequency, the output voltage V_{out} simply equals $I_{in} R_b$. The value of L should be chosen in such a way that the resonance frequency occurs at a relatively low value that can easily be processed by the voltage follower of Fig. 5 and the subsequent read-out apparatus.

Fig. 4. The equivalent circuit of the conductance cell with a series inductor.

Fig. 5. Constant-current mode of operation for the conductance cell with an added inductor.

Experimental

Details of the processing and manufacturing of the conductance cell are given in ref. 2. Basically, the cell consists of two chips of 5 mm × 5 mm, positioned face to face with a 5 mm wide spacer in between. Each chip is a sandwich of an Si/SiO₂ substrate, a 250 nm thick Au film (the metallic electrode of C_{ox}) and an approximately 110 nm thick Ta₂O₅ film.

Measurements were carried out in a KCl solution at room temperature (21 ± 2 °C). The KCl concentration was varied between 0.2 and 100 mM, and the corresponding specific resistances ρ were obtained from standard tables [5]. The cell constant K was determined from previous measurement results: $K = 1.05 \text{ cm}^{-1}$ [2]. Consequently, the resistance $R_b = \rho K$ to be expected ranged from ≈ 30 to 15 k Ω .

Results and discussion

Oscillator mode

Measurements were carried out with the circuit, shown in Fig. 3. Because of the lowest value for R_b that is possible, a resistor of 7.5 k Ω was placed in series with the cell in order to guarantee oscillation. For the other components, $C_x = 1.5 \text{ nF}$ and $R_x = 570 \text{ k}\Omega$ were chosen. The value of C_{ox} of Fig. 1 was estimated to be $C_{ox} = \epsilon_0 \epsilon_r A/d \approx 25 \text{ nF}$ ($A = 16 \text{ mm}^2$, $\epsilon_r \approx 20$). The experimental results are given in Fig. 6.

The change in the slope of the measured curve in Fig. 6, after the initial linear behaviour for concentrations higher than 10 mM, is mainly caused by the extra resistor of 7.5 k Ω is series with the conductance cell. This extra component eventually causes the curve to approach asymptotically a maximum value of the frequency. Another reason for this behaviour is that the relative change in specific resistance slightly decreases per decade change in concentration for higher

Fig. 6. Experimental results of the conductance cell operated in the oscillator mode.

Fig. 7. Experimental results of the conductance cell operated in the pole mode.

electrolyte concentrations due to the decreased mobility of ions.

The pole mode

Measurements were carried out with the circuit, shown in Fig. 5. For the inductor, L , a value of 800 μH was chosen, resulting in a theoretical value for f_{res} of 50 kHz. Experimentally, the minimum in the output voltage of the circuit, $V_{out} = I_{in}/R_b$, was found at 53 kHz, indicating a reasonably precise control over the process parameters, especially the thickness d of the Ta₂O₅ film. For the measurements a current $I_{in} = 30 \mu\text{A}_{rms}$ was used. The results of measurements of KCl concentrations ranging from 0.2 to 100 mM are shown in Fig. 7.

The results show that a linear change in electrolyte resistance (here represented by $V_{out} = I_{in}/R_b$) per decade of electrolyte concentration, as theoretically expected, is obtained within the measured range.

Conclusions

Two new modes of operation are proposed, which are especially suited for the previously introduced Ta₂O₅-based conductance probe.

In the oscillator mode, the conductance cell is utilized as the frequency determining part of an oscillator. Although the initial results show the feasibility of this mode, the design of the oscillator should be optimized in order to enlarge the operating range.

With the pole mode, an inductance is placed in series with the conductance cell. At the resonance frequency, only the electrolyte resistance determines the electrical behaviour of the total circuit. The measurement results show the expected linear behaviour over almost three

decades without varying any of the values of the other circuit components.

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