A new probe for measuring electrolytic conductance

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Abstract

A conductance cell of which the electrodes are provided with a 110 nm thick Ta_2O_5 insulating film is proposed and realized. The stable and very low impedance of the total oxide/solution interface largely reduces interference from redox processes. Measurement results, given as an output voltage between 10 and 600 mV as a function of the specific resistance between 0.1 and 8 kΩ, are shown to be in agreement with theoretically calculated results, both at the constant current and constant voltage mode of operation.

1. Introduction

Electrolytic conductance measurements are nowadays carried out easily with commercially available equipment. While modern sensor technology shows ongoing miniaturization, the existing probes for measuring conductance are still relatively large. Simply decreasing the dimensions of the applied electrode configuration is often impossible and is not compatible with modern, planar sensor technology.

Therefore, a new conductance measuring probe requires a new design. Apart from the dimensions, the choice of the electrode material and interface electrochemistry are some of the parameters to be considered when optimizing the new design. Both the dimensions and the electrode material are discussed in this paper. In addition, it is demonstrated that the choice of the controlling electronic circuitry greatly influences the result of an accurate conductance measurement with this probe.

1.1. The measuring probe

Conventionally, measurements of electrolytic conductance are carried out with inert metal electrodes, e.g., Pt. A schematic representation of one half of an electrolytic conductance cell is depicted in Fig. 1(a) [1].

In Fig. 1(a), Z_f represents the faradaic impedance, C_{dl} the double-layer capacitance and R_b the resistance of the electrolyte. Z_f and C_{dl} do not behave as ideal electronic components. The value of C_{dl} is a function of the concentration of the electrolyte and the faradaic impedance Z_f is a rather complex component, which represents the possible electrochemical reactions at the electrode/solution interface. These reactions cause noise
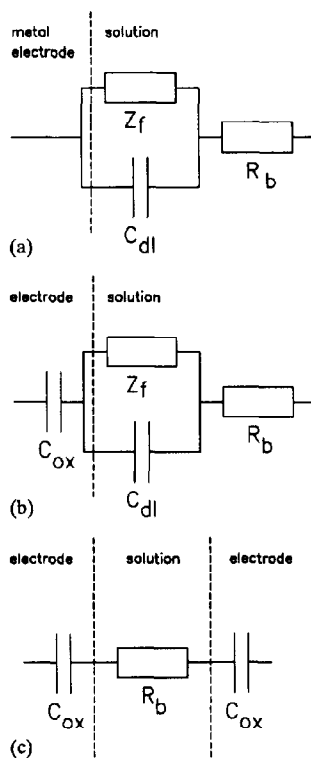

Fig. 1. Schematic representation of the conductance cell: (a) one half of the cell; (b) one half of the cell with insulating film; and (c) simplified representation of the total cell.

on the electric signal of the metal electrode. The impedance Z_f is a function of the potential over the interface, the concentration and composition of the electrolyte as well as the frequency of the a.c. potential.

Many paper (e.g., refs. 2–4) propose refinements either in signal handling or in shape and treatment of the metal electrodes in order to minimize the effects of the non-ideal components of Fig. 1(a). In this paper, a different approach is proposed, namely, the use of a thin layer of insulating tantalum pentoxide deposited on top of the conducting electrode. This material was chosen because it is known from literature concerning ISFETs [5] that the Ta_2O_5/solution interface has a stable, relatively low impedance Z_f, which is even lower than the double-layer impedance and is almost totally determined by the activity of protons in the solution. Therefore, noise caused by interfering redox processes is largely reduced.

The price to be paid is the introduction of an extra component, shown in Fig. 1(b) as C_{ox}. However, the dielectric constant of Ta_2O_5 is very high: $\epsilon_r \approx 20$. The capacitance C_{ox} of a 4×4 mm^2 capacitor ($A = 16$ mm^2) with an oxide thickness $d \simeq 110$ nm is $C_{ox} = \epsilon_0 \epsilon_r A / d \simeq 25$ nF.

By choosing the operating frequency of the cell in such a way that the reactance of the total oxide/solution impedance is much smaller than that of the oxide capacitance, $|C_{ox}|$, it effectively behaves like a short circuit and the total conductance cell can be represented by Fig. 1(c). The total impedance of this cell is

$$Z_{cell} = \frac{2 + j\omega R_b C_{ox}}{j\omega C_{ox}} = R_b - j\frac{2}{\omega C_{ox}} \tag{1}$$

and is no longer dependent on C_{dl} or Z_f as given in Fig. 1(a).

1.2. The electronic circuit

The conductance cell can be operated in two different modes: constant current and constant potential.

1.2.1. Constant current

With the circuit as shown in Fig. 2(a), the cell operates in the constant current mode and the potential over the cell is measured with a voltage follower, having a very high input impedance and a gain of unity. The modulus of the transfer v_{out}/i_{in} is

$$\left|\frac{v_{out}}{i_{in}}\right| = |Z_{cell}| = \left[R_b^2 + \frac{4}{(\omega C_{ox})^2}\right]^{1/2}$$

$$= \frac{1}{\omega C_{ox}}[(\omega C_{ox} R_b)^2 + 4]^{1/2} \tag{2}$$

If $(\omega C_{ox} R_b) \gg 2$, then eqn. (2) can be simplified to $|v_{out}/i_{in}| = R_b$.

1.2.2. Constant voltage

With the circuit as shown in Fig. 2(b), the cell operates in the constant voltage mode and the current through the cell is measured with a current-to-voltage converter,
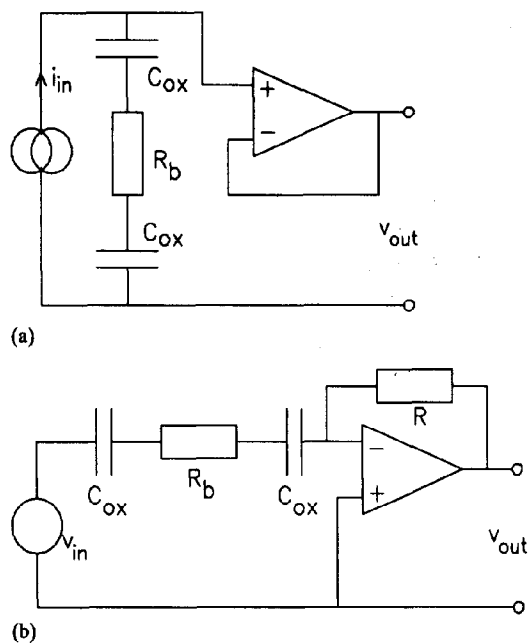

(a)

(b)

Fig. 2. Electronic circuit for the (a) constant current and (b) constant voltage mode.

having a low input impedance and a transfer $v_{out}/i = -R$. The modulus of the transfer v_{out}/v_{in} is

$$\left|\frac{v_{out}}{v_{in}}\right| = \frac{\omega R C_{ox}}{[(\omega C_{ox} R_b)^2 + 4]^{1/2}} \tag{3}$$

If $(\omega C_{ox} R_b) \gg 2$, then eqn. (3) can be simplified to $|v_{out}/v_{in}| = R/R_b$.

2. Experimental

2.1. The conductance cell

A 250 nm thick Au film was evaporated by resistive heating on top of a 2 inch Si wafer with 0.6 μm SiO_2. In between the SiO_2 and the Au film was a 30 nm thick Ti film for adhesion. This Au film forms the metal electrode of C_{ox}, shown in Fig. 1(c).

Then, 50 nm Ta was applied on top of the Au film by e-gun evaporation with a deposition rate of 3 Å/s. This Ta film was oxidized at 550 °C for 2 h in O_2 ambient, resulting in a Ta_2O_5 layer of approximately 110 nm. Openings to the Au electrode were accomplished by reactive ion etching of the Ta_2O_5 through a photolithographically determined mask.

After the wafer was diced to 5×5 mm^2 chips, these chips were glued on 8×100 mm^2 printed circuit board carriers and the Au electrode was connected to the copper strips on the PCB with bonding wires. The copper strips, the bonding wires and the edges of the chip were covered with epoxy for insulating and pro-

tection. A cross section of the chip is shown in Fig. 3.

Two of these dipsticks were glued together, face to face, with a 5 mm wide spacer in between, forming the total conductance cell.

2.2. The measurement set-up

All a.c. signals were sinusoidal with a frequency of 200 kHz and are presented in r.m.s. values. The constant current i_{in} of the current source in Fig. 2(a) was 20 μA and the constant voltage v_{in} in Fig. 2(b) was 100 mV. The OpAmp in the circuit of Figs. 2(a) and (b) was a Model CA3140 (RCA). Measurements were carried out in a KCl solution at room temperature (21 ± 2 °C).
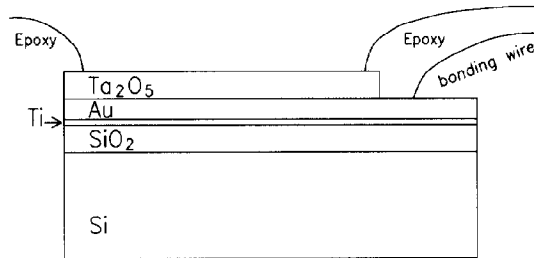

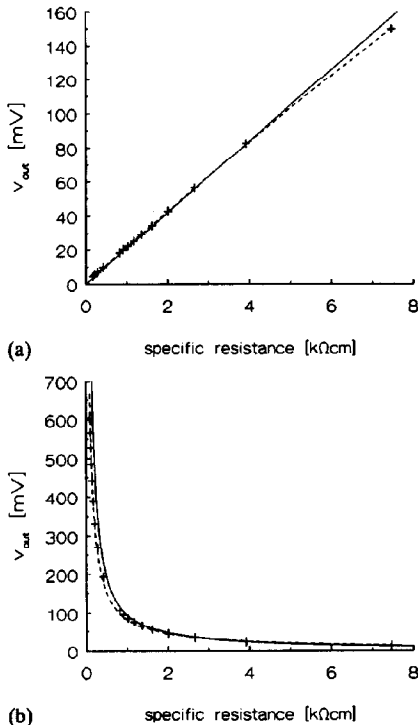Fig. 3. Cross section of the electrode.

(a)   specific resistance [kΩcm]

(b)   specific resistance [kΩcm]

Fig. 4. Measurement results (– – –) and theoretical calculations (eqns. (2) and (3), ——) of the capacitive conductance cell of (a) constant current and (b) constant potential source.

3. Results and discussion

Measurements were carried out with the conductance cell as described in the previous sections, with the circuits as shown in Fig. 2. The KCl concentration was varied between 1 and 100 mM and the corresponding specific conductances were obtained from standard tables [6].

The results of these measurements both for the constant current and the constant voltage mode of operation are shown in Figs. 4(a) and (b), respectively.

Note, that on the horizontal axes of Figs. 4(a) and (b), the specific resistance ρ (kΩ cm) is placed instead of the specific conductance σ (mS/cm) ($\rho = 1/\sigma$). This is done in order to make comparison with eqns. (2) and (3) easier. The relation between the specific resistance ρ of the electrolyte and R_b of Figs. 1(c) and 2, and eqns. (1)–(3) is given by [1]

$$R_b = \rho K = K/\sigma \tag{4}$$

where K (cm^{-1}) is the so-called cell constant of the conductivity cell, which depends on the electrode surface area A, the spacing between the measuring electrodes l and a form factor k, correcting the effects of the inhomogeneous electrical field between the two electrodes due to the edges: $K = kl/A$.

The cell constant K was determined from the measurement results of Fig. 4(a): $K = 1.05$ cm^{-1}. With this cell constant and eqn. (4), the theoretical curve according to eqn. (2) could be calculated and is also shown in Fig. 4(a). This cell constant was also used to calculate the theoretical curve according to eqn. (3) for the constant potential mode. This curve is shown in Fig. 4(b).

Depending on the range of interest and the subsequent processing of the data, one of the proposed modes, constant current ($v_{out} = f(\rho)$ is linear) or constant potential ($v_{out} = f(\rho)$ is sensitive for low ρ), can be favourable.

Further research will be focused on miniaturization of this cell.

4. Conclusions

A probe for measuring electrolytic conductance has been proposed with a low impedance oxide/solution interface, that reduces interfering effects from redox processes.

The cell can operate in both the constant current and the constant voltage mode and it has been shown that the measurement results are in agreement with the theoretically expected behaviour of the cell.

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