

Dielectric properties of anodic oxide layers on tantalum

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The dielectric properties of the anodically formed oxide layers on tantalum in contact with electrolyte were analysed by measuring the frequency and temperature dependence of the impedance. It has been found that the frequency dependence of the series capacitance and resistance component of the impedance in the audio frequency range are in accordance with Young's relation. In order to explain such behaviour the electrical resistivity is assumed to vary exponentially with distance through the oxide layer. This variation can be ascribed to the occurrence of the exponential change of oxygen vacancies in the anodic layer during the growth of the oxide layer. The activation energy was obtained from the temperature dependence of the series capacitance. In the paper the unsimplified Young's relations have been proved to be K-K transformable.

Nomenclature

C_s series capacitance (F)
 R_s series resistance (Ω)
 f frequency of applied signal (Hz)
 x integration variable of frequency (Hz)
 A area (cm^2)
 K characteristic length (cm^{-1})
 d oxide layer thickness (cm)
 y distance through oxide (cm)
 a_C slope of linear part of $1/C_s$ against $\log f$ plot (Equation 5)

a_R slope of linear part of R_s against $1/f$ plot (Equation 3)
 ϵ relative permittivity of oxide layer
 $\rho(y)$ resistivity at distance y ($\Omega \text{ cm}$)
 $\rho(0)$ resistivity on position $y = 0$ ($\Omega \text{ cm}$)
 $\rho(d)$ resistivity on position $y = d$ ($\Omega \text{ cm}$)
 T absolute temperature (K)
 k Boltzmann constant (eV K^{-1})
 ϕ activation energy (eV)
 z complex variable, $z = x + iy$, $i = \sqrt{-1}$
 Res residue

1. Introduction

A study of the electrical properties of tantalum pentoxide is of great interest because of its application in the electronic industries [1]. Tantalum oxide may serve as an alternative dielectric to SiO_2 for metal/oxide/semiconductor (MOS) structures [2, 3] due to its high relative permittivity, thus obtaining a greater storage capacitance for the same thickness of the oxide layer. Oxide layers anodically formed on tantalum are generally non-stoichiometric and are amorphous in structure [4]. The structure and non-stoichiometry essentially affect the electric properties of the oxide layers on tantalum. Information on the dielectric properties of the metal/oxide/electrolyte (MOE) structures can be obtained by impedance measurements. The results of impedance measurements are generally expressed in terms of series resistance, R_s , and series capacitance, C_s , which are frequency dependent in most electrochemical systems. In order to explain the frequency dependence of the real and imaginary component of impedance Young [5] has derived equations showing the dependence of R_s and $1/C_s$ on frequency on

the basis of a model in which the resistivity varies exponentially across the oxide layer, i.e. $\rho(y) = \rho(0) \exp(y/K)$.

The equivalent circuit representing the layer consists of an infinite number of parallel RC units connected in series. Young has ascribed the exponential variation of resistivity to the deviation from the stoichiometry of the niobium oxide. Young's relation between the resistance and frequency is given by

$$R_s(f) = \frac{18 \times 10^{11} K}{\epsilon A f} \left[\arctan \left(\frac{f \epsilon \rho(d)}{18 \times 10^{11}} \right) - \arctan \left(\frac{f \epsilon \rho(0)}{18 \times 10^{11}} \right) \right] \quad (1)$$

and between the capacitance and frequency by

$$\frac{1}{C_s(f)} = \frac{\pi \times 18 \times 10^{11} K}{\epsilon A} \ln \left[\frac{1 + \left(\frac{f \epsilon \rho(d)}{18 \times 10^{11}} \right)^2}{1 + \left(\frac{f \epsilon \rho(0)}{18 \times 10^{11}} \right)^2} \right] \quad (2)$$

Assuming that the resistance is low on one side and high on the other side of the oxide, i.e. $\rho(d) \gg \rho(0)$, Equations 1 and 2 may be simplified as follows:

$$R_s = a_R(1/f) + b \quad (3)$$

or

$$\log(R_s - b) = \log a_R - \log f \quad (4)$$

A conversion of Equation 2 to a logarithm of base 10 yields

$$\frac{1}{C_s} = a_C \left[\log f + \log \left(\frac{\epsilon \rho(d)}{18 \times 10^{11}} \right) \right] \quad (5)$$

The additive constant b in Equation 3 is mostly associated with the electrolyte resistance. Young's expressions, (3) and (5), state that the resistance is a linear function of the reciprocal frequency and capacitance is a linear function of the logarithm of frequency. Theoretically, the ratio of the respective slope is

$$\frac{a_C}{a_R} = 9.2 \quad (6)$$

The fact that the values a_C/a_R , which were experimentally obtained on the oxide-coated Nb electrode, were in agreement with the theoretical values (Equation 6) supports Young's model. Winkel and de Groot [6] had another theoretical approach to describe the impedance behaviour on oxide-coated Ta and Al electrodes and they obtained the same expressions. These authors assumed the distribution of relaxation times in the oxide. The Equations (3) and (5) were found to describe the electrode impedance on oxide-coated Ti electrodes [7], on anodized Al in nonaqueous medium [8], on the passive layer on iron in contact with CrO_3 solution [9, 10], on polished TiC electrodes under anodic polarization [11], on oxide-coated Pt [12] and on thermally grown oxide films on iron [13]. The results presented in the papers [8–13] were interpreted on the basis of Young's or Winkel and de Groot's models. Dutoit *et al.* [14] have established that the relations 3 to 5 are also valid for nearly ideally polarisable semiconducting electrodes: CdS, CdSe and TiO_2 monocrystals. The same relations were obtained with n- and p-type GaAs [15]. These authors [14, 15] also explained the simple Equations 3 and 5 by means of a model where the distribution of the time constant is associated with the dielectric relaxation phenomena in the double layer at the semiconductor/electrolyte interface.

In this paper, the a.c. electrical properties of the anodically formed layers on tantalum in contact with an electrolyte will be discussed. On the tantalum/oxide layer/electrolyte system the impedance was measured by comparing it with the series combination of capacitance, C , and resistance, R , in the bridge.

2. Experimental details

Electrodes were prepared from spectroscopically clean tantalum rods (Johnson-Matthey), 4.5 mm dia., which

were sealed into glass tubes with epoxy resin. The exposed disc faces were polished with Buchler metallographic powder and degreased in trichlorethylene. The tantalum samples were anodized at a constant current density, $j_f = 1 \text{ mA cm}^{-2}$ up to a formation voltage, $U_f = 5 \text{ V}$ and 40 V in $1.0 \text{ mol dm}^{-3} \text{ Na}_2\text{SO}_4$ solution at room temperature. The samples were stabilized for 48 h at the formation voltage. The oxide layer thicknesses (for the constant current stage) were computed from tantalum anodization constant which amounts to 1.75 nm V^{-1} [16]. The increment of 30% [17] of the thickness, which is due to the relatively long soak time, was added to the value computed from the anodization constant, so that the final thicknesses of the oxide layers were 11.4 nm and 91 nm. The bridge method was used to measure the impedance of the Ta/oxide layer/electrolyte system. The superimposed a.c. signal was obtained using a Hewlett-Packard 3300A function generator. The voltage at the bridge ends amounted to 10 mV. The impedance was measured within a frequency range between 250 Hz and 25 kHz and at temperatures ranging from 274 K to 314 K without d.c. polarization.

3. Results and discussion

The capacitance and resistance of anodically formed layers on tantalum for $U_f = 5 \text{ V}$ and 40 V are presented as $1/C_s$ against $\log f$ and R_s against $1/f$ with temperature as parameter (Figs 1–4). Within the frequency range 250 Hz–10 kHz the reciprocal capacitance increases linearly with the logarithm of frequency (Figs 1 and 2), and the resistance increases linearly with the reciprocal frequency (Figs 3 and 4) at all temperatures, which is in agreement with relations (3)

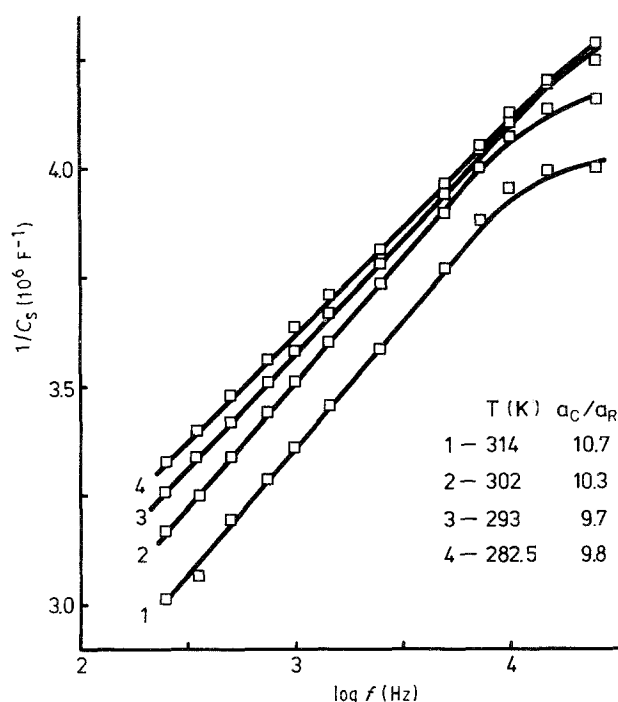


Fig. 1. Reciprocal series capacitance against logarithm of frequency for various temperatures in open circuit. Oxide layer formed with $j = 1 \text{ mA cm}^{-2}$ up $U_f = 5 \text{ V}$ in $1.0 \text{ mol dm}^{-3} \text{ Na}_2\text{SO}_4$ solution.

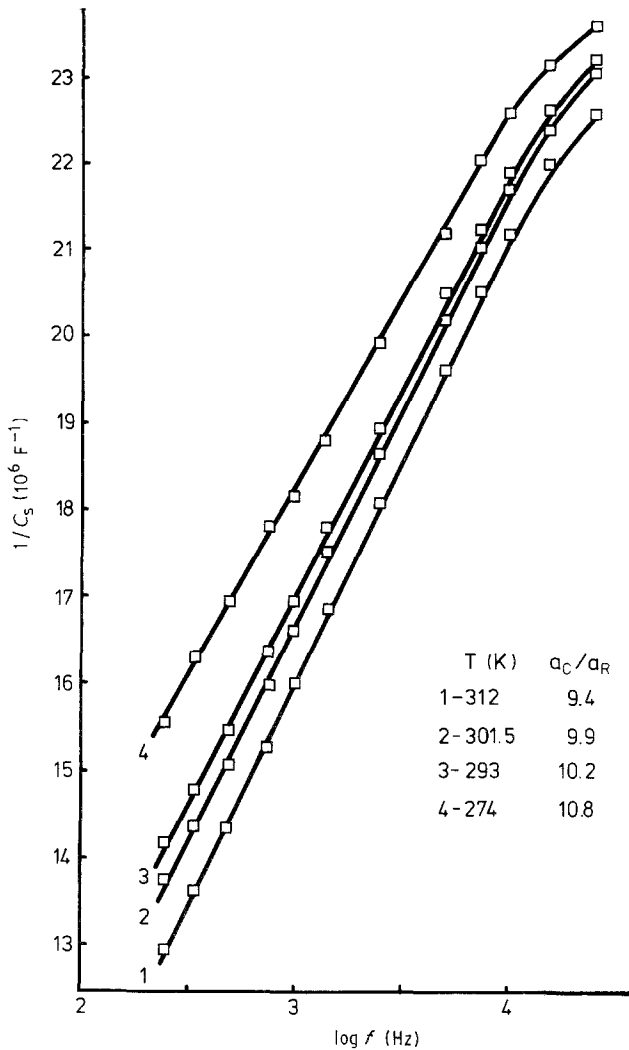


Fig. 2. Reciprocal series capacitance against logarithm of frequency for various temperatures in open circuit. Oxide layer formed with $j = 1 \text{ mA cm}^{-2}$ up $U_j = 40 \text{ V}$ in $1.0 \text{ mol dm}^{-3} \text{ Na}_2\text{SO}_4$ solution.

and (5). The slopes a_C and a_R (Equations 3 and 4) were determined from the line of linear regression. The ratios of temperature dependent slopes a_C/a_R are shown in the inset of Figs 1 and 2 and are in agreement with Young's theoretical value (Equation 6). To establish the influence of the electrolyte resistance for each temperature, a linear part of the (R_s against $1/f$) plot was extrapolated at $1/f = 0$ and the values obtained

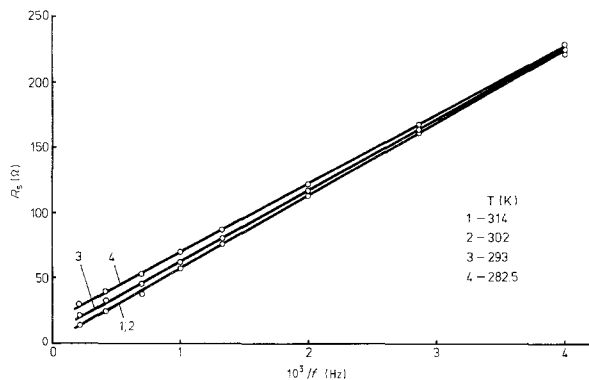


Fig. 3. Series resistance against reciprocal frequency for various temperatures in open circuit. Oxide layer formed with $j = 1 \text{ mA cm}^{-2}$ up $U_j = 5 \text{ V}$ in $1.0 \text{ mol dm}^{-3} \text{ Na}_2\text{SO}_4$ solution.

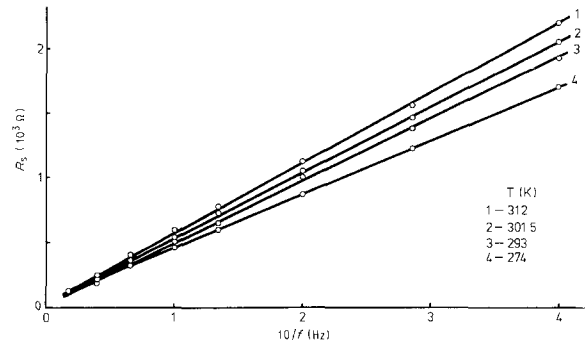


Fig. 4. Series resistance against reciprocal frequency for various temperatures in open circuit. Oxide layer formed with $j = 1 \text{ mA cm}^{-2}$ up $U_j = 40 \text{ V}$ in $1.0 \text{ mol dm}^{-3} \text{ Na}_2\text{SO}_4$ solution.

for the electrolyte resistance, R_{el} , were subtracted from the measured values R_s . The results are presented as $\log(R_s - R_{el})$ against $\log f$ in Figs 5 and 6. At all temperatures, this plot represents a linear relationship in agreement with Equation 4. The slopes are temperature independent for both thicknesses of the oxide layer and the values $(R_s - R_{el})$ at a certain frequency vary negligibly with temperature. The slopes are -1 which is in excellent agreement with Equation 4 (see inset of Figs 5 and 6).

Considering the problems of the frequency dependence of the electrode impedance. Van Meirhaeghe *et al.* [18] point out that under certain conditions, the frequency dependence of the real and imaginary components of the electrical impedance is sometimes correlated by the Kramers-Kronig (K-K) relation [19, 20]. In the case of impedance defined by

$$Z = R_s - i \frac{1}{2\pi f C_s} \quad (7)$$

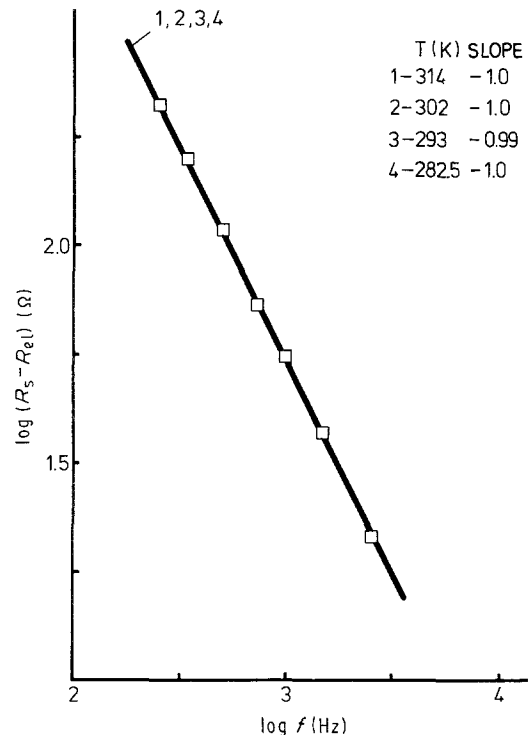


Fig. 5. Logarithm of series resistance against logarithm of frequency for various temperatures in open circuit. Oxide layer formed with 1 mA cm^{-2} up $U_j = 5 \text{ V}$ in $1.0 \text{ mol dm}^{-3} \text{ Na}_2\text{SO}_4$ solution.

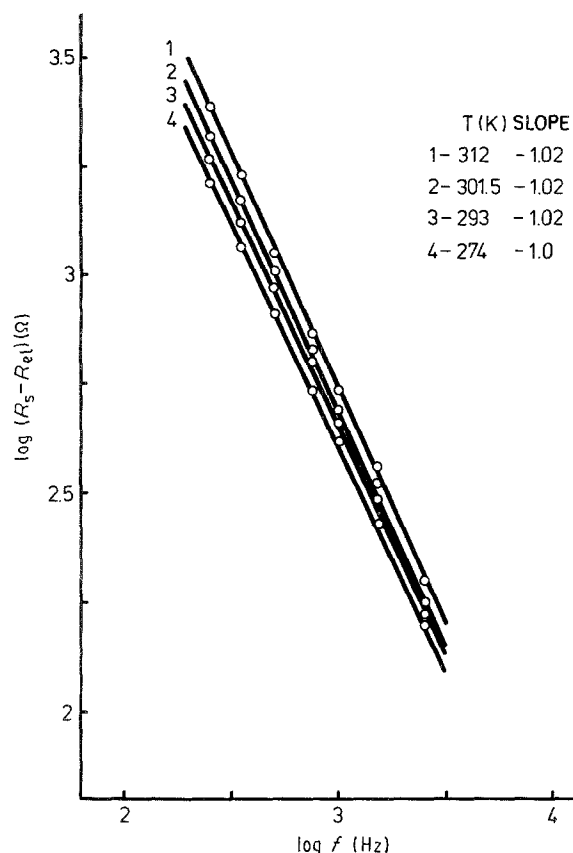


Fig. 6. Logarithm of series resistance against logarithm of frequency for various temperatures in open circuit. Oxide layer formed with $j = 1 \text{ mA cm}^{-2}$ up $U_f = 40 \text{ V}$ in $1.0 \text{ mol dm}^{-3} \text{ Na}_2\text{SO}_4$ solution.

the Kramers-Kronig or Bode relations [18, 21] are often presented in various forms, one of them being

$$\frac{1}{C_s(f)} = -4f^2 \int_0^\infty \frac{R_s(x)}{x^2 + f^2} dx \quad (8)$$

and

$$R_s(f) - R_s(\infty) = \frac{1}{\pi^2} \int_0^\infty \frac{1/C_s(x)}{x^2 - f^2} dx \quad (9)$$

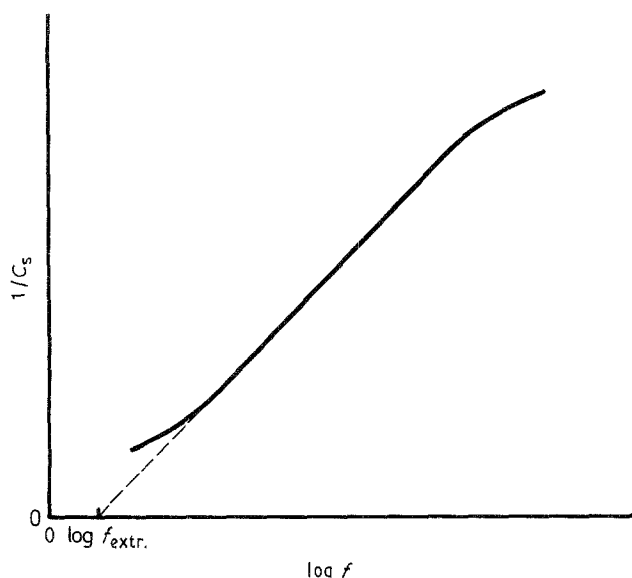


Fig. 7. The shape of the curve $1/C_s$ against $\log f$ in a wide range of frequencies.

where \int denotes the Cauchy principal value of the integral. K-K relations are a purely mathematical result and can be obtained from the properties of continuous functions of the complex variable. To be applicable to an electrical quantity (such as impedance) the quantity must be causal, linear, stable and finite at all frequencies including $f = 0$ and $f = \infty$. The consequence of the K-K relations is such that if the real part of the impedance is known in the entire frequency range, its imaginary part is uniquely determined, and when the imaginary part is given, the real part is completely determined up to the additive constant $R(\infty)$.

Van Meirhaeghe *et al.* [18] have shown that by inserting Equation 3 into the integral Equation 8, the solution is Equation 5 if R_s is assumed to tend to a constant when $f \rightarrow 0$; otherwise an infinite value of the integral is obtained. However, if Young's Equation 1 is inserted into the integral Equation 8, the solution is:

$$\begin{aligned} \frac{1}{C_s(f)} &= -4f^2 B \left[\int_0^\infty \frac{\arctan(Dx)}{x^2 - f^2} dx \right. \\ &\quad \left. - \int_0^\infty \frac{\arctan(Ex)}{x^2 + f^2} dx \right] \\ &= \pi B \ln \left[\frac{1 + D^2 f^2}{1 + E^2 f^2} \right] \end{aligned} \quad (10)$$

where

$$B = \frac{18 \times 10^{11} K}{\epsilon A} \quad (11)$$

$$D = \frac{\epsilon \rho(d)}{18 \times 10^{11}} \quad \text{and} \quad E = \frac{\epsilon \rho(0)}{18 \times 10^{11}} \quad (12)$$

Inserting Equation 2 into the Equation 9 gives:

$$\begin{aligned} R_s(f) - R_s(\infty) &= \frac{B}{\pi} \left[\int_0^\infty \frac{\ln(1 + D^2 f^2)}{x^2 - f^2} dx \right. \\ &\quad \left. - \int_0^\infty \frac{\ln(1 + E^2 f^2)}{x^2 - f^2} dx \right] \\ &= \frac{B}{f} [\arctan(Df) - \arctan(Ef)] \end{aligned} \quad (13)$$

The integrals on the left hand side of Equations 10 and 13 respectively, have been solved by applying Cauchy's residue theorem (see Appendix, Equations A-7 and A-15).

For low frequencies, provided that $\rho(d) \gg \rho(0)$, Equation 2 is of the form

$$\frac{1}{C_s(f)} = \pi B \ln(1 + D^2 f^2) \quad (14)$$

Since $(1 + D^2 f^2) > 1$ always when $f \rightarrow 0$, the linear part of the plot $1/C_s$ against $\log f$ becomes nonlinear, approaching asymptotically to zero or some other constant value if there is a capacitance connected in series with the layer capacitance where Young's relations (Equations 1 and 2) are valid

(Fig. 7) [22]. Inserting Equation 14 into Equation 9 for the limiting condition $f \rightarrow 0$, a simple expression is obtained

$$R_s(0) - R_s(\infty) = \frac{B}{\pi} \int_0^\infty \frac{\ln(1 + D^2 x^2)}{x^2} dx \quad (15)$$

and hence

$$R_s(0) - R_s(\infty) = \frac{K}{A} \rho(d) \quad (16)$$

Integral 15 is also solved by using Cauchy's residue theorem (see Appendix, Equation A-20). From Equation 16 it follows that if the impedance measurements are carried out in a sufficiently wide frequency range and if the capacitance component behaves in accordance with Equation 14, the resistance component for the limiting condition $f \rightarrow 0$ tends to a constant value (Equation 16). Equating the left hand side of Equation 5 to zero it follows that [10]

$$\frac{1}{f_{\text{extr}}} = \frac{\varepsilon \rho(d)}{18 \times 10^{11}} \quad (17)$$

or

$$\log \rho(d) = \log \left(\frac{18 \times 10^{11}}{\varepsilon} \right) - \log f_{\text{extr}} \quad (18)$$

The term f_{extr} in Equation 17 can be obtained by extrapolating the linear part of the $1/C_s$ against $\log f$ plot at $1/C_s = 0$ (Fig. 7).

Such an analysis was carried out on the data shown in Figs 1 and 2. The linear part was extrapolated at $1/C_s = 0$ for each temperature and the resistivity, $\rho(d)$, was calculated using Equation 17. A value of $\varepsilon = 27.8$ [23] was used for the permittivity of tantalum oxide. The logarithm of resistivity was plotted against $1/T$ for both oxide layer thicknesses (Fig. 8). This plot yields straight lines and, from the slopes, the activation energy was calculated by the Arrhenius-type expression

$$\Phi = \frac{k}{0.4343} \frac{d \log [\rho(d)]}{d [1/T]} \quad (19)$$

The activation energy was 0.9 eV for the thinner layer and 0.52 eV for the thicker layer.

The results presented in this paper are consistent with the assumption that in the anodic oxide layers on tantalum, the conductivity is exponentially dependent on the position in the oxide layer, and that it decreases from the maximum value which is most probably achieved on the tantalum/oxide layer interface until it reaches the lowest value on the oxide/electrolyte interface. The exponential variation of the conductivity may be associated with the existence of the exponential distribution of the oxygen vacancies in the anodic oxide layer, which occurred during the growth of the oxide layer.

Capacity measurements have revealed that the capacitance is potential independent. This means that a possible space charge layer has a thickness at least larger than the film itself. K-K transformability of Young's relations (Equations 1 and 2) does not favour

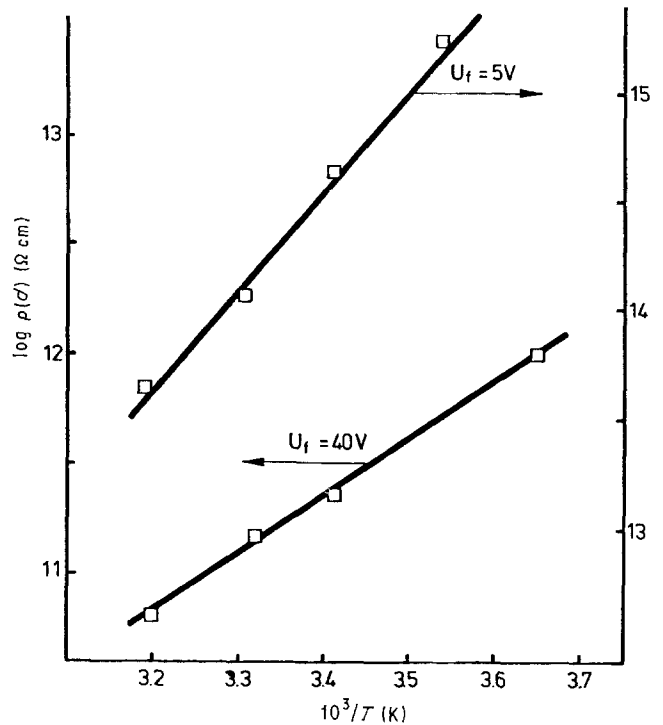


Fig. 8. Logarithm of specific resistivity against reciprocal temperature for oxide layers formed with $j = 1 \text{ mA cm}^{-2}$ up $U_f = 5$ and 40 V in $1.0 \text{ mol dm}^{-3} \text{ Na}_2\text{SO}_4$ solution.

this model as opposed to others, since these relations are a purely mathematical result, which does not reflect any other physical property or condition of the electrochemical system. It would therefore be possible to suppose an alternative model which could be explained by a distribution of relaxation times (DRFs) [6]. The analysis of relaxation processes in dielectric materials often starts from the empirical Cole-Cole response function which gives a relationship between dielectric permittivity and relaxation times ([24], Equation 5). This relationship implies the independence of phase angle (or loss angle) on frequency. Experimental results show that R_s varies as $1/f$ in the audio frequency range (Figs 3 and 4) so that the phase angle can be constant only if C_s is frequency independent. Results in Figs 1 and 2 show that this is not the case.

4. Conclusions

This study of the dielectric properties of the anodic oxide layers on tantalum in contact with electrolyte shows that the resistivity depends exponentially on position in the oxide layer. The electric resistivity is related to the local deviation from tantalum oxide stoichiometric composition. The conductivity is thermally activated and the activation energy amounts to 0.9 eV for the thinner layer and 0.53 eV for the thicker layer. These values are in close agreement with the activation energy values obtained on the heat-treated anodic layers on tantalum [25, 26]. Young's relations (Equations 1 and 2) describing the behaviour of the capacitance and the resistance component of the impedance in the entire frequency range are proved to be K-K transformable.

Appendix

The integrals on the left hand side of Equations 10, 13 and 15 are solved by applying Cauchy's residue theorem. The integration is made along the semicircle which lies in the upper half of the complex plane and whose diameter is a part of the real axis (Figs A-1, A-2 and A-3). The simple poles $x = \pm f$ and $x = 0$ which lie on the real axis $\{z | \text{Im } z = 0\}$ are excluded from the region of integration so that the functions under consideration are analytic everywhere within the closed contour C , and the contour integral along C is thereby zero. The interal along the semicircle at infinity is also zero.

To compute the integral

$$\int_0^\infty \frac{\arctan x}{x(x^2 - f^2)} dx \quad f > 0 \quad (\text{A-1})$$

the contour from Fig. A-1 and expression given in [27] (p. 122) are used

$$\begin{aligned} \int_0^\infty f(x) \cdot \arctan x \, dx &= -\pi \sum_{k=1}^n \text{Res } f(z) \ln(i + z) \\ &\quad - \frac{\pi}{2} \sum_{k=1}^n \text{Res } \ln(i + z) \end{aligned} \quad (\text{A-2})$$

where z_k is a finite number of singular points in the region $\{z | \text{Im } z > 0\}$, and p_k are simple poles on the real axis $\{z | \text{Im } z = 0\}$.

The function

$$f(z) = \frac{1}{z(z^2 - f^2)}$$

on the real axis $\{z | \text{Im } z = 0\}$ has three simple poles, $p_1 = 0$, $p_2 = -f$ and $p_3 = f$, the residues of which are

$$\text{Res}_{z=0} \frac{\ln(i + z)}{z(z^2 - f^2)} = -i \frac{\pi}{2f^2} \quad (\text{A-3})$$

$$\text{Res}_{z=f} \frac{\ln(i + z)}{z(z^2 - f^2)} = \frac{\ln(i + f)}{2f^2} \quad (\text{A-4})$$

$$\text{Res}_{z=-f} \frac{\ln(i + z)}{z(z^2 - f^2)} = \frac{\ln(i + f)}{2f^2} \quad (\text{A-5})$$

The first sum on the right hand side of expression (A-2) is zero because the function is analytical. In other words, it does not involve singular points z_k in the region $\{z | \text{Im } z > 0\}$.

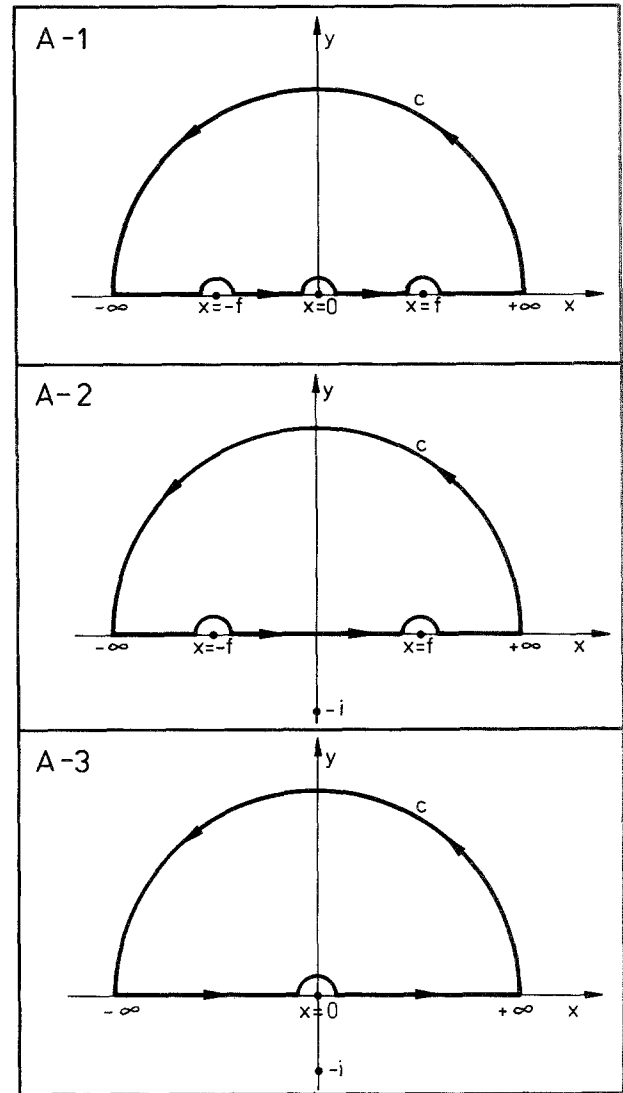
By inserting (A-4) up to (A-5) into the expression (A-2) we obtain

$$\int_0^\infty \frac{\arctan x}{x(x^2 - f^2)} dx = -\frac{\pi}{4} \frac{\ln(1 + f^2)}{f^2} \quad (\text{A-6})$$

or

$$\int_0^\infty \frac{\arctan(cx)}{x(x^2 - f^2)} dx = -\frac{\pi}{4} \frac{\ln(1 + c^2 f^2)}{f^2} \quad (\text{A-7})$$

where c is a constant.



The integral

$$\int_0^\infty \frac{\ln(1 + x^2)}{x^2 - f^2} dx \quad f > 0 \quad (\text{A-8})$$

can be solved by splitting the numerator of the integrand into partial fractions and using the property of the even function, i.e. $f(x) = f(-x)$, yields

$$\begin{aligned} \frac{\ln(1 + x^2)}{x^2 - f^2} &= \frac{\ln[(x + i)(x - i)]}{x^2 - f^2} \\ &= \frac{2 \ln(x + i) + i\pi}{x^2 - f^2} \end{aligned} \quad (\text{A-9})$$

Inserting the left hand side of expression (A-9) into (A-8), we obtain

$$\begin{aligned} \int_0^\infty \frac{\ln(1 + x^2)}{x^2 - f^2} dx &= 2 \int_0^\infty \frac{\ln(x + i)}{x^2 - f^2} dx \\ &\quad + i\pi \underbrace{\int_0^\infty \frac{dx}{x^2 - f^2}}_{=0} \end{aligned} \quad (\text{A-10})$$

To solve the first integral on the right hand side in (A-10), the contour on Fig. A-2 and expression given

in [27] (p. 124) are used

$$2 \int_0^{\infty} f(x) \ln(i+x) dx = 2i\pi \sum_{k=1}^n \operatorname{Res} f(z) \ln(i+z) + i\pi \sum_{k=1}^n \operatorname{Res} f(z) \ln(i-z) \quad (\text{A-11})$$

The function

$$f(z) = \frac{1}{x^2 - f^2}$$

on the real axis $\{z | \operatorname{Im} z = 0\}$ has two single poles, $p_1 = f$ and $p_2 = -f$, the residues of which are

$$\operatorname{Res}_{z=f} \frac{\ln(i+z)}{x^2 - f^2} = \frac{\ln(i+f)}{2f} \quad (\text{A-12})$$

$$\operatorname{Res}_{z=-f} \frac{\ln(i+z)}{x^2 - f^2} = \frac{\ln(i-f)}{2f} \quad (\text{A-13})$$

Since the function $z \rightarrow \ln(i+z)$ is analytic in the upper half plane $\{z | \operatorname{Im} z > 0\}$ because the singular point $z = -i$ is outside the contour, the first sum on the right hand side of Equation A-11 is zero. By inserting Equations A-12 and A-13 into Equation A-11 we obtain

$$\int_0^{\infty} \frac{\ln(1+x^2)}{x^2 - f^2} dx = \frac{\pi}{f} \arctan f \quad (\text{A-14})$$

or

$$\int_0^{\infty} \frac{\ln(1-c^2x^2)}{x^2 - f^2} dx = \frac{\pi}{f} \arctan(cx) \quad (\text{A-15})$$

The integral

$$\int_0^{\infty} \frac{\ln(1-x^2)}{x^2} dx \quad (\text{A-16})$$

is solved in the same way as integral A-8. The integrand is an even function, that is:

$$\int_0^{\infty} \frac{\ln(1+x^2)}{x^2} dx = 2 \int_0^{\infty} \frac{\ln(i+x)}{x^2} dx + \underbrace{i\pi \int_0^{\infty} \frac{dx^2}{x^2}}_{=0} \quad (\text{A-17})$$

To solve the first integral on the right hand side in Equation A-17 the contour from Fig. A-3 and Equation A-11 are used.

The function

$$f(z) = \frac{1}{z^2}$$

on the real axis $\{z | \operatorname{Im} z = 0\}$ has a pole of order two, $p = 0$, and its residue is

$$\operatorname{Res}_{z=0} \frac{\ln(i+z)}{z^2} = \frac{1}{i} \quad (\text{A-18})$$

By inserting Equation A-18 into Equation A-11 it follows that

$$\int_0^{\infty} \frac{\ln(1+x^2)}{x^2} dx = \pi \quad (\text{A-19})$$

$$\int_0^{\infty} \frac{\ln(1+c^2x^2)}{x^2} dx = c\pi \quad (\text{A-20})$$

References

- [1] R. W. Berry, P. H. Hall and M. T. Harris, 'Thin Film Technology', Van Nostrand, Princeton (1968).
- [2] R. L. Angie and H. E. Talley, *IEEE Trans. Electron Devices* **ED-25** (1978) 1277.
- [3] T. Kallfass and E. Lueder, *Thin Solid Films* **61** (1979) 259.
- [4] L. Young, 'Anodic Oxide Films', Academic Press, New York (1961).
- [5] L. Young, *Trans. Faraday Soc.* **51** (1955) 1250.
- [6] P. Winkel and D. G. de Groot, *Philips Res. Rep.* **13** (1958) 489.
- [7] E. G. Kuznetsova, T. J. Borisova and V. I. Veselovskii, *Elektrokhimiya* **4** (1968) 167.
- [8] W. J. Bernard, *J. Electrochem. Soc.* **108** (1961) 446.
- [9] B. Lovreček and B. Jarić, 4th Int. Congr. Metallic Corrosion, Amsterdam (1969). Extended abstracts.
- [10] B. Jarić, O. Korelić and B. Lovreček, Proc. 5th Int. Congr. Metallic Corrosion, Tokyo (1972).
- [11] I. Paseka, *Coll. Czech. Chem. Commun.* **39** (1974) 1974.
- [12] J. Clavilier and C. R. Pineaux, *Acad. Sc. Paris* **260** (1965) 891.
- [13] K. S. Yun, S. M. Wilhelm, S. Kapusta and N. Hackerman, *J. Electrochem. Soc.* **127** (1980) 85.
- [14] E. C. Dutoit, R. L. Van Meirhaeghe, F. Cardon and W. P. Gomes, *Ber. Bunsenges. Physik. Chem.* **79** (1975) 1206.
- [15] W. H. Laflère, R. L. Van Meirhaeghe, F. Cardon and W. P. Gomes, *Surf. Sci.* **59** (1976) 401.
- [16] G. C. Wood and C. Pearson, *Nature* **208** (1965) 547.
- [17] J. M. Albella, I. Montero, O. Sanchez and J. M. Martinez-Duart, *J. Electrochem. Soc.* **133** (1986) 87.
- [18] R. L. Van Meirhaeghe, E. C. Dutoit, F. Cardon and W. P. Gomes, *Electrochim. Acta* **21** (1976) 39.
- [19] H. A. Kramers, *Physiol. Zool.* **30** (1929) 522.
- [20] R. de L. Kronig, *J. Opt. Soc. Am.* **12** (1926) 547.
- [21] H. W. Bode, 'Network Analysis and Feedback Amplifier Design', Van Nostrand, New York (1945).
- [22] B. Jarić, Ph.D. Thesis, Faculty of Technology, University of Zagreb (1969).
- [23] L. Young, *Proc. Roy. Soc. Lond. Ser. A.* **244** (1958) 41.
- [24] K. S. Cole and R. H. Cole, *J. Chem. Phys.* **9** (1941) 341.
- [25] D. M. Smyth, G. A. Shirn and T. B. Tripp, *J. Electrochem. Soc.* **111** (1964) 1331.
- [26] D. M. Smyth and G. A. Shirn, *ibid.* **115** (1968) 186.
- [27] D. S. Mitrinović and J. D. Kečkić, 'Cauchy's Calculus of Residues with the Applications' (Cauchijev račun ostataka s aplikacijama), Naučna Knjiga, Beograd (1978). (In Serbian.)