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ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY INVESTIGATIONS OF TANTALUM AND ITS PASSIVE FILMS IN SOME ACIDIC SOLUTIONS

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În această lucrare, a fost utilizată spectroscopia de impedanţă electrochimică pentru a studia creşterea filmelor de oxid pe tantal în soluţii de acid oxalic, sulfuric şi azotic. A fost investigat de asemenea efectul potenţialului de formare al filmelor anodice, a densităţii de curent de formare şi a naturii chimice a mediului de pasivare asupra proprietăţilor filmelor de oxid de tantal. Rezultatele arată o bună stabilitate a filmelor de oxid în diverse medii acide.

In this paper, electrochemical impedance spectroscopy was used to study the growth of thin oxide films on tantalum in aqueous solutions of oxalic, sulfuric and nitric acid. The effect of formation voltage, formation current density and the nature of passivation medium on the properties of the anodic tantalum oxide films were also investigated. The results show a good stability of these films in various acid media.

Keywords: Tantalum, passive film, electrochemical impedance, acid media

1. Introduction

The electrochemical behavior of valve metals is of high scientific and technical value because of their implications in the manufacture of electrolytic capacitors and growing of passivating layers in electronics as well as protective and decorative films [1,2,3]. The Intel's newest series of processors (i7) use the hafnium oxide in their technologies [4]. In this series, tantalum is an important valve metal and its oxidation was subject of numerous investigations [2-3, 5,6,7] in view of potential use of tantalum oxide for capacitors.

Although advanced electroceramics such as various titanates show higher dielectric constants (*e.g.* $BaTiO_3$), it is very difficult to integrate these materials as thin films into electronic devices. The anodic oxide formation on valve metals such as Al, Ta, Nb and Ti may be a suitable technique for producing very thin oxide films. Thus, the best capacitance-volume ratio is obtained by electrolytic

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capacitors based on Nb_2O_5 and Ta_2O_5. Several electrochemical techniques as polarization curves, potentiodynamic curves, electrochemical quartz crystal microbalance, have been used to study the anodic behavior of tantalum [7-8,9]. Electrochemical Impedance Spectroscopy (EIS) has provided new information concerning the behavior of anodic films on Al [10], Zr [11], Ti [12] and Ta [13]. It was shown that the main advantage of EIS technique is the data processing using an electrical circuit as model to represent the behavior of electrode/electrolyte interface. Thus, an interface undergoing an electrochemical reaction is analogous to an equivalent circuit consisting in a combination of resistors and capacitors.

The aim of the present EIS investigation is to obtain more information concerning the formation and stability of thin anodic films formed on Ta. The effect of film thickness, formation current density and growth medium on the electrochemical behavior of the thin film covered electrode was also investigated.

2. Experimental

The measurements were carried out using a classical three-electrode cell. The working electrode was made from a 99.9% tantalum rod (Goodfellow) with an exposed surface area of $3.14 mm^2$. A platinum mesh was auxiliary electrode. The electrode potentials were measured against a saturated Ag/AgCl electrode. The electrolytic solutions of oxalic, sulfuric and nitric acids were prepared using analytical grade (p.a.) reagents and Millipore water (conductivity $\approx 18.2 M\Omega \cdot cm$). Before each determination, the tantalum electrode was polished using 0.04 μm alumina suspension (Leco), washed extensively with water and dried. The anodic film was grown galvanostatically in the test solution at various current densities. An impedance measurement was performed immediately after immersion of tantalum electrode, followed by anodic oxidation during a time interval of. Then, when the desired formation potential was achieved the film growth was interrupted and a new impedance measurement was performed at the open-circuit potential. This procedure was repeated for various formation voltages, up to 10V.

The impedance of the electrochemical system was determined using a PGSTAT 12 system (Metrohm Autolab,). A 10 mV amplitude a.c. signal and a frequency range between 0.05 Hz and l MHz were normally used. All experiments were carried out at room temperature (23±2°C).

3. Results and discussion

3.1. Behavior of the bare Ta metal in acid solutions

The EIS results obtained with the bare tantalum (without anodization) in 0.25M $H_2C_2O_4$, 0.25M H_2SO_4 and 0.5M HNO_3 solutions are presented as Bode diagrams in Fig. 1. The initial impedance was measured at 15-20 seconds after electrode immersion and has the minimum value for each acid medium; in the following EIS determinations it increases continuously up to a value where 10V formation potential is reached. This increase of impedance is attributed to a progressive formation of oxide film [14]. Moreover, the open-circuit potential shifted continuously to more positive values with time, illustrating the complete passivation of Ta surface. This behavior is certainly because the native film formed is too thin to ensure a good protection [15]. The healing and further thickening of this film by the formation of a thin tantalum oxide will occur until a steady state is achieved.

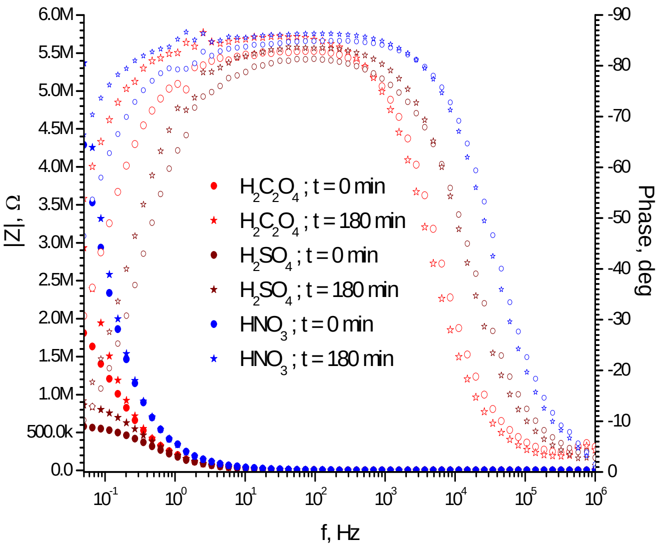

Fig. 1. Bode EIS spectra of bare Ta metal in oxalic (0.25M), sulfuric (0.25M) and nitric (0.5M) acid solutions.

Also, Bode diagrams show a large frequency region of the maximum phase angle which has values higher than 85°, closed to the 90° value corresponding to an ideal capacitor behavior.

The knowledge of the total thickness of layer is very important for calculating the dielectric constant (relative permittivity) of the tantalum oxide. A possible approach is the linear plot of the reciprocal capacitance (C^{-1}) versus the layer thickness d [16]. The native oxide thickness (before anodization) can be estimated from this plot as the intersection with the x-axis at $C^{-1} = 0$. In this calculation the measured overall capacitance (see the sum of three terms in Eq. 1) can be regarded as approximately equal to the capacitance of the anodic film, only [17]:

$$\frac{1}{C} = \frac{1}{C_{ox/me}} + \frac{1}{C_{ox}} + \frac{1}{C_{ox/el}} \approx \frac{1}{C_{ox}} \qquad (1)$$

In the above equation, $C_{ox/me}$ is the capacitance of the metal/oxide film interface which is usually negligible. C_{ox} is the capacitance of oxide layer. $C_{ox/el}$ is the Helmholtz capacitance of the oxide/electrolyte layer (double layer) and its value commonly used in literature is 20-30 $\mu F \cdot cm^{-2}$ [18]; this capacitance can be also neglected in eq. (1), since $C_{ox} << C_{ox/el}$ [19].

All results of initial EIS measurements do not indicate more than one time constant, RC, a parameter that has a constant value in time for each acid medium. Therefore, the impedance spectra can be interpreted quite well by a simple equivalent circuit as a model of the interface between tantalum electrode and acid electrolyte. This electrical circuit is represented in fig. 2, where R_s is the electrolyte resistance, and R_{ox} and C_{ox} are the resistance and capacity of the anodic oxide film, respectively.

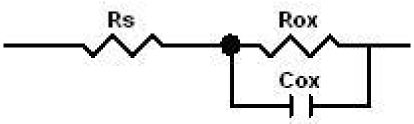

Fig. 2. The proposed equivalent electrical circuit corresponding to Ta/Ta_2O_5/electrolyte interface.

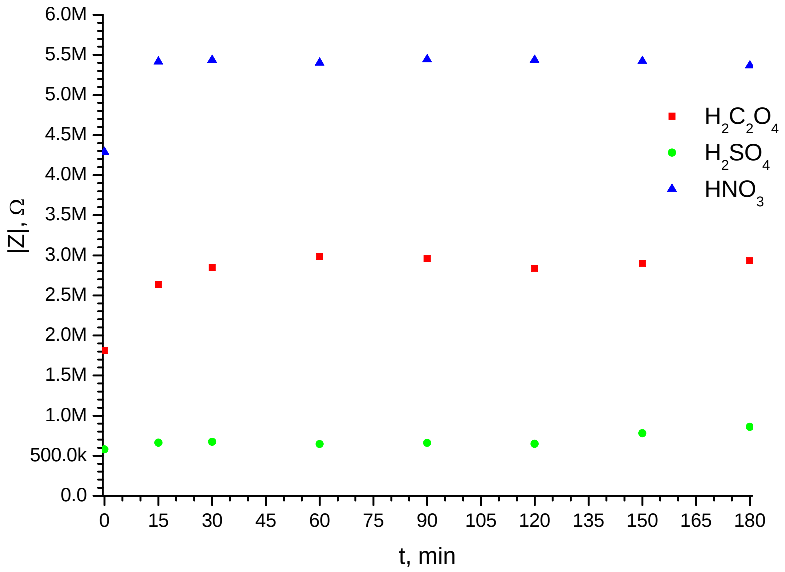

Fig. 3. |Z| vs. time for bare metal

In Fig. 3 and Fig. 4 it appears that, following a short induction period (tipically in the range of 15-30 min), the total impedance and the RC time constant of the native film become horizontal straight lines; this is a typical behavior for a valve metal coated with a native oxide film.

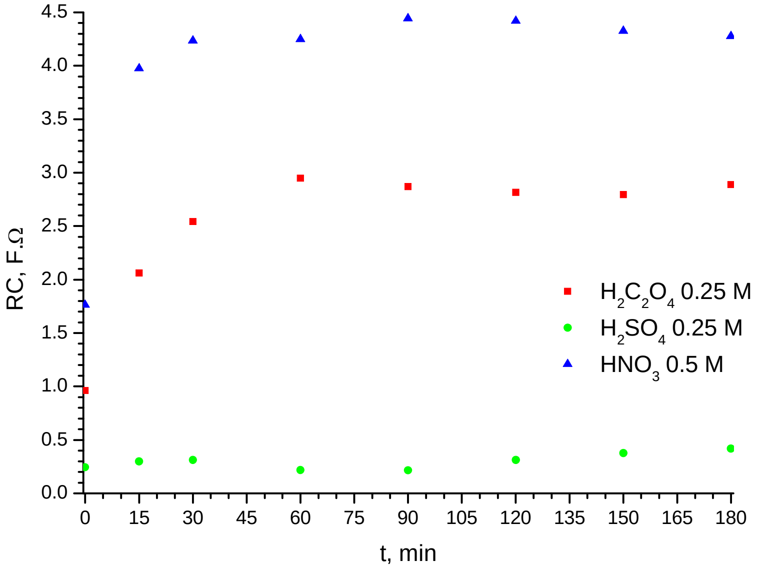

Fig. 4. RC vs. time for bare metal

3.2. Behavior of passive film on tantalum electrode

The evolution of impedance characteristics of the tantalum electrode having passive film at initial moment of immersion in electrolytes and after film thickening in the same acid solutions is presented in fig. 5.

A comparison of |Z| values of bare (Fig. 1) and covered (Fig. 5) electrodes shows a more than one order of magnitude higher values for covered electrode. Also, a great difference in the behavior of phase angle at highest frequencies between Fig. 5 and Fig. 1 is noticed, because for covered electrode the phase angle remains constant and identical in value (85-88 degrees) for all acids; this is typical for a thin, compact, insulating layer of anodic oxide film. Phase angle values at very low frequencies are comparable (between two Figures).

For a given insulating oxide layer, the reciprocal capacitance, C^{-1}, is directly proportional to its thickness d [14]. The value of reciprocal capacitance, C^{-1}, can be obtained either from the Bode plot at a frequency of 0.159Hz where the impedance data give a straight line with a slope of ≈ -1 or from the value of the imaginary part of impedance, Z_{im}, at the same frequency (0.159Hz) using the

Eq. 2 [11]:

$$\frac{1}{C} = \omega \cdot Z_{im} = 2\pi \cdot 0.159 \times Z_{im} \tag{2}$$

From this reciprocal capacitance of anodic film, C^{-1}, one can estimate the film thickness using the well known expression of plan capacitors:

$$d = \frac{\varepsilon \cdot \varepsilon_0 \cdot A}{C} \tag{3}$$

where *d* is the total (i.e., including the “native”) film thickness; in the eq.(2) ε is the dielectric constant of Ta_2O_5 which is taken equal to 27.5 [20], ε_0 the permittivity of vacuum ($8.85 \cdot 10^{-14}$ $F \cdot cm^{-1}$) and A is the exposed area of the electrode.

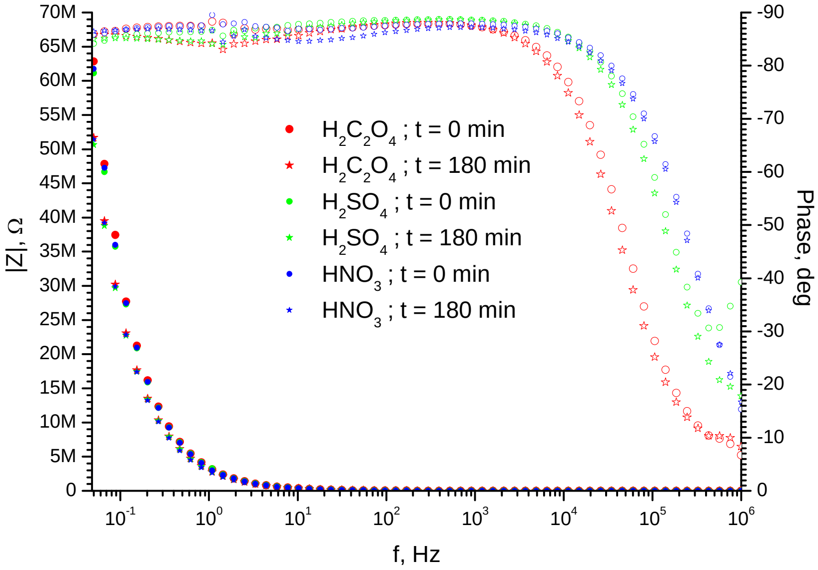

Fig. 5. Bode EIS spectra of covered tantalum (parameters: $j = 1 mAcm^{-2}$; $E_f = 10$ V vs. Ag/AgCl) in oxalic (0.25M), sulfuric (0.25M) and nitric (0.5M) acid solutions.

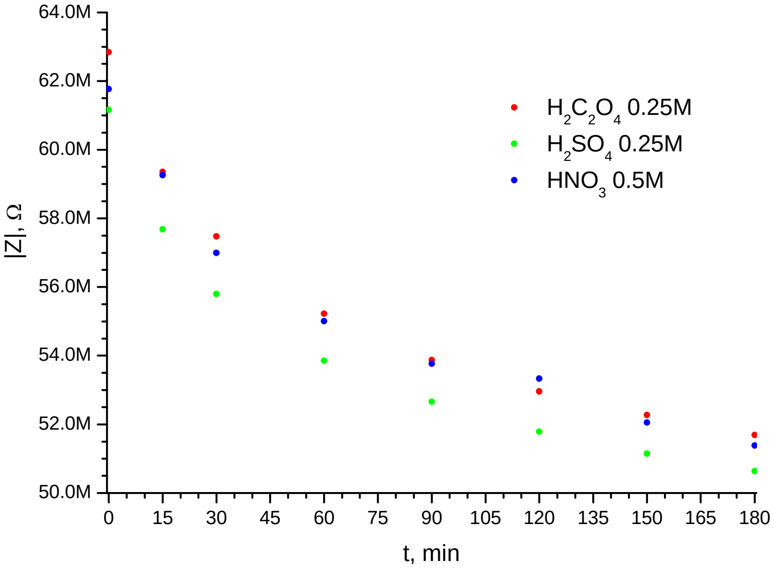

Fig. 6. |Z| vs. time for behavior test of covered tantalum (parameters: j = 1mAcm^{-2} ; E_f = 10 V vs. Ag/AgCl) in oxalic (0.25M), sulfuric (0.25M) and nitric (0.5M) acid solutions.

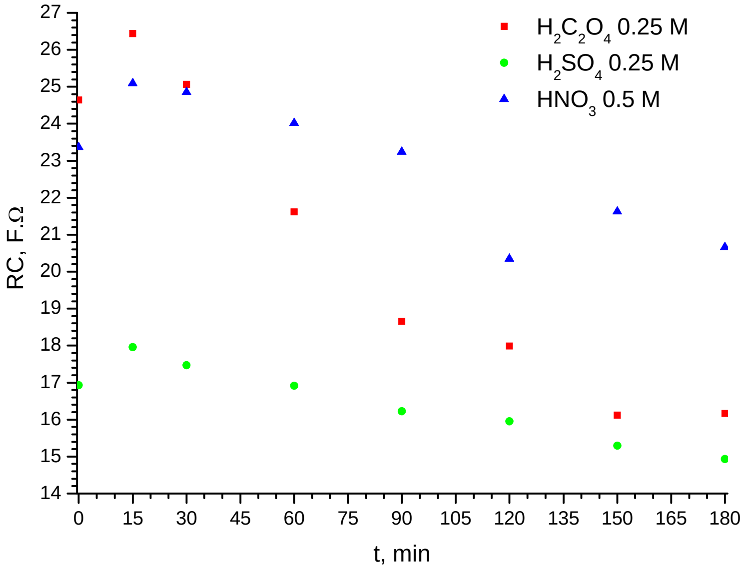

Fig. 7. RC vs. time for covered tantalum

3.2.1. Effect of formation voltage on the stability of the passive film on Ta

To investigate the stability of the anodic oxide films formed on Ta in various acid solutions (naturally aerated), impedance measurements were carried out after galvanostatic formation of the passive film at a certain current density. After passivation up to the desired formation potential, the electrode was quickly connected to the EIS system and the measurements were performed in the same solution.

To study the effect of formation voltage, oxide films were formed up to the voltage reached values of 2, 4, 6, 8 and 10V, as described in experimental section. The EIS results obtained with the Ta electrode passivated in 0.25M $H_2C_2O_4$, 0.25M H_2SO_4 and 0.5M HNO_3 solutions up to formation potential of 10 V and tested in the same solution were presented in Fig. 5. The impedance values increase as the formation voltage increases; this is due to the oxide film thickening. The spectra show that there are small changes in the impedance values with time which may be linked to subtle changes in the oxide film [14]. Also, the value of the phase angle almost maximum, $\theta_{max} \approx 90°$ (ca. 2°-5° less) indicates that the passive film thus formed on Ta approaches ideal capacitor behavior. The chemical nature of acid solution does not show remarkable effect on the behavior of the passivated electrode, i.e. similar results were obtained when the test solution is $H_2C_2O_4$, H_2SO_4 or HNO_3.

The relation of C^{-1} and d vs. time gave the straight lines which can be represented by Eq. 4a and Eq. 4b, respectively:

$$\frac{1}{C} = \frac{1}{C_o} + b \cdot t \tag{4a}$$

$$d = d_o + b' \cdot t \tag{4b}$$

where b or b' depends on the nature of the electrolyte, concentration and the time of immersion, and C_0^{-1} is the reciprocal capacitance at zero time which is a measure of the initially formed anodic oxide film thickness d_0. Our results show that the extent of the oxide film dissolution is very low; this means that the anodic oxide film formed on Ta is very stable. The values of C_0^{-1} and d_0 for different formation voltages were obtained by extrapolation of C_0^{-1} and d vs. time plots to zero time. It was found that both C^{-1} and d increase linearly with formation voltage, which means that anodic oxide films on Ta grow linearly with increasing anodic potential. The point when the slope changes its value in the straight line relationship between C^{-1} and time (or d and time) indicates that the rate of oxide film thickening on tantalum changes after certain time (30 minutes in our case).

The values of C^{-1} and d for the tantalum electrode were calculated at different time intervals, after the growth was interrupted. Fig. 8 and Table 1 and Fig. 9 and Table 2 show the corresponding curves for variation of C^{-1} and d with immersion time, t, for oxalic acid and sulfuric acid, respectively.

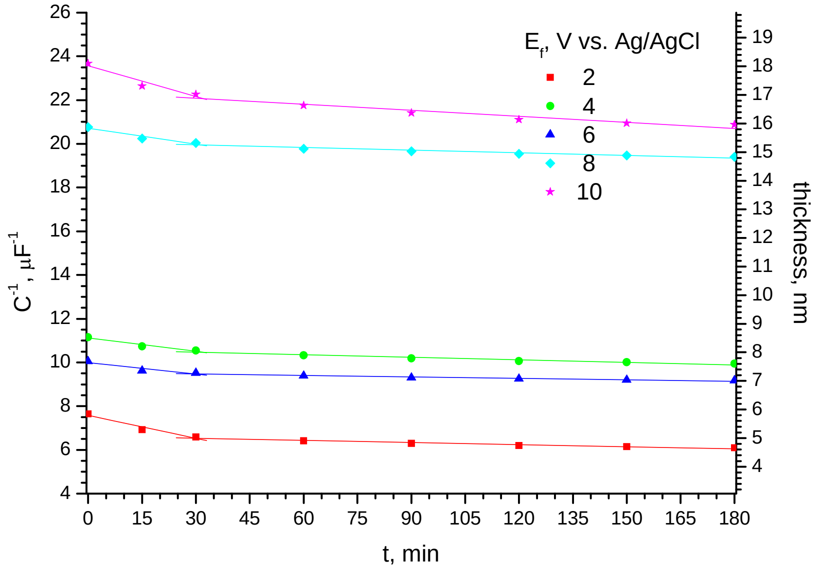

Fig. 8. C^{-1} vs. time and thickness vs. time; $C_2H_2O_4$ 0.25 M, 0.5 mA·cm^{-2}

Table 1. C^{-1} vs. time and thickness vs. time for $C_2H_2O_4$ 0.25M.

j, mA·cm^{-2}	E_f, V vs. Ag/AgCl	a_1, µF^{-1}	$b_1 \cdot 10^2$, µF^{-1}·min^{-1}	a_2, µF^{-1}	$b_2 \cdot 10^3$, µF^{-1}·min^{-1}
0.5	2	7.58	-3.49	6.63	-3.26
	4	11.12	-2.02	10.59	-3.92
	6	9.99	-1.75	9.54	-17.54
	8	20.71	-2.44	20.07	-4.00
	10	23.57	-4.70	22.36	-9.23
1.0	2	6.16	-2.99	5.29	-2.52
	4	10.89	-5.49	9.43	-5.84
	6	11.88	-7.24	10.02	-3.20
	8	18.97	-2.25	18.44	-3.61
	10	24.39	-4.61	23.18	-5.62
2.5	2	7.63	-2.64	6.95	-4.15
	4	11.16	-3.78	10.13	-5.51
	6	14.72	-3.05	13.89	-3.43
	8	18.56	-2.47	17.96	-4.60
	10	25.39	-2.73	24.69	-4.53

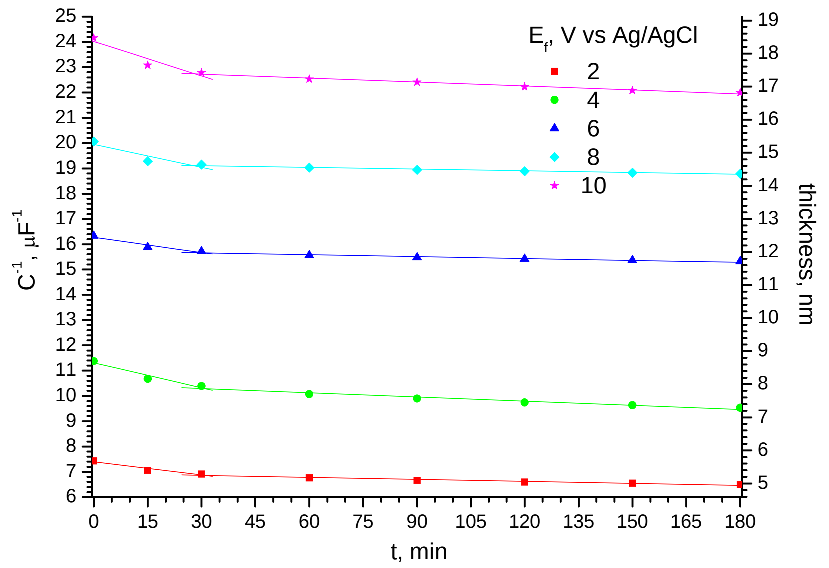

Fig. 9. C^{-1} vs. time and thickness vs. time; H_2SO_4 0.1M, E_f = 10V/AgCl, 1 mA·cm^{-2}

Table 2. C^{-1} vs. time and thickness vs. time for H_2SO_4 solutions, E_f = 10V/AgCl, 1 mA·cm^{-2}.

Concentration, M	**E_f, V vs. Ag/AgCl**	**a_1 , μF^{-1}**	**$b_1 \cdot 10^2$, $\mu F^{-1} \cdot min^{-1}$**	**a_2 , μF^{-1}**	**$b_2 \cdot 10^3$, $\mu F^{-1} \cdot min^{-1}$**
0.1	2	7.39	-1.72	6.94	-2.64
	4	11.31	-3.31	10.45	-5.50
	6	16.28	-2.02	15.74	-2.52
	8	19.95	-3.04	19.18	-2.29
	10	24.02	-4.55	22.89	-5.20
0.25	2	6.99	-1.14	6.73	-2.15
	4	11.72	-1.89	11.23	-3.21
	6	15.66	-3.10	14.82	-3.37
	8	19.62	-3.86	18.63	-5.37
	10	23.98	-4.79	22.78	-7.66
0.5	2	7.52	-1.14	7.22	-2.13
	4	11.33	-2.46	10.67	-2.78
	6	15.97	-2.08	15.44	-2.69
	8	20.12	-4.62	18.94	-6.81
	10	24.09	-4.24	23.04	-7.25

3.2.2. Effect of formation current density

Anodic oxide films were formed up to 10 V vs. Ag/AgCl at different current densities of 0.5, 1, and 2.5mA·cm^{-2}. The electrodes were then transferred to the medium which is the same solution. Fig. 10 and Table 3 shows that the oxide film formed at lower current density is more stable than that formed at higher current density. The decrease in the passive film stability by increasing the formation current density is probably due to the increasing number of defects in the oxide film matrix [5].

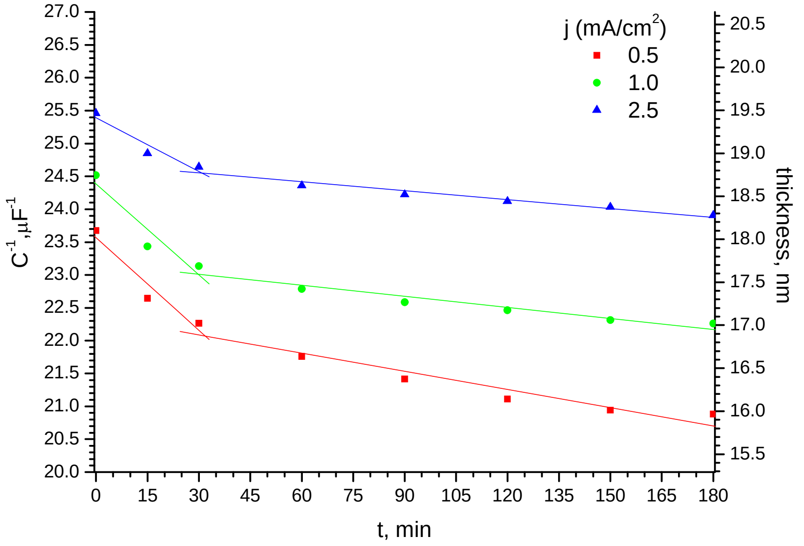

Fig. 10. C^{-1} vs. time and thickness vs. time; $H_2C_2O_4$ 0.25M, E_f = 10V/AgCl

Table 3. Effect of formation current density.

media	j, mA·cm^{-2}	a_1, µF^{-1}	$b_1 \cdot 10^2$, µF^{-1} ·min^{-1}	a_2, µF^{-1}	$b_2 \cdot 10^3$, µF^{-1} ·min^{-1}
$H_2C_2O_4$ 0.25M	0.5	23.57	-4.70	22.36	-9.23
	1.0	24.39	-4.61	23.18	-5.62
	2.5	25.39	-2.73	24.69	-4.53
H_2SO_4 0.25M	0.5	26.43	-1.83	25.98	-2.02
	1.0	23.98	-4.79	22.78	-7.66
	2.5	24.10	-3.32	23.19	-4.41
HNO_3 0.5M	0.5	26.34	-5.24	24.98	-9.60
	1.0	24.58	-3.99	23.54	-7.51
	2.5	22.72	-4.14	21.64	-7.65

3.2.3. Effect of the passivation medium acid nature on film stability

In the experiments, anodic oxide films were formed in a sufficient anodization time until 10V formation potential; the current densities were 0.5, 1 and 2.5mAcm^{-2} in 0.25M H_2SO_4, 0.25M $H_2C_2O_4$ and 0.5M HNO_3 solutions. After reaching 10V formation potential, the current was interrupted, and the EIS measurements were performed at 15 min time intervals. The results of reciprocal capacitance vs. time are presented in Fig. 11 and Table 4. The high stability of the anodic oxide film in the corresponding test solution demonstrated the formation of a highly ordered and less defective tantalum oxide film.

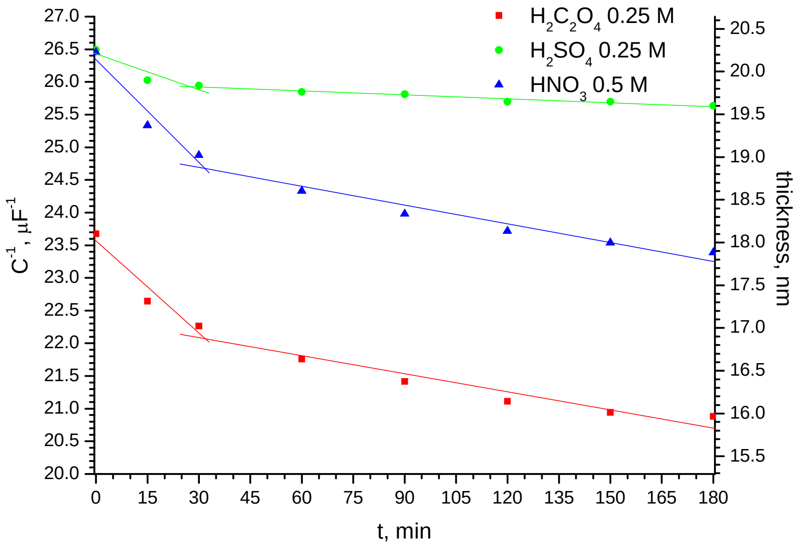

Fig. 11. C^{-1} vs. time and thickness vs. time; E_f = 10V/AgCl; j = 0.5 mA·cm^{-2}

Table 4

Effect of the passivation medium acid nature

j, mA·cm^{-2}	media	a_1 , μF^{-1}	$b_1 \cdot 10^2$, μF^{-1}·min^{-1}	a_2 , μF^{-1}	$b_2 \cdot 10^3$, μF^{-1}·min^{-1}
0.5	$H_2C_2O_4$ 0.25M	23.57	-4.70	22.36	-9.23
	H_2SO_4 0.25M	26.43	-1.83	25.98	-2.02
	HNO_3 0.5M	26.34	-5.24	24.98	-9.60
1.0	$H_2C_2O_4$ 0.25M	24.39	-4.61	23.18	-5.62
	H_2SO_4 0.25M	24.58	-3.99	23.54	-7.51
	HNO_3 0.5M	23.98	-4.79	22.78	-7.66
2.5	$H_2C_2O_4$ 0.25M	25.39	-2.73	24.69	-4.53
	H_2SO_4 0.25M	22.72	-4.14	21.64	-7.65
	HNO_3 0.5M	24.10	-3.32	23.19	-4.41

4. Conclusions

Tantalum forms passive films in sulfuric, nitric and oxalic acid aqueous solutions under open-circuit conditions and 0.1-0.5M concentrations. These highly stable anodic oxide films can be obtained by using low current density (0.5 $mA\cdot cm^{-2}$) for nitric or sulfuric acid as formation medium or using high current density (2.5 $mA\cdot cm^{-2}$) for oxalic acid as formation medium.

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