ELECTROCHEMICAL AND IMPEDANCE CHARACTERIZATION OF PASSIVE FILMS ON NIOBIUM IN ALKALINE AND ACIDIC SOLUTIONS

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In this work electrochemical characterization of the anodic passive films formed on Nb in alkaline (0.1 – 5 M KOH) and acidic solution (H_2SO_4) was carried out by cyclic voltammetry and electrochemical impedance spectroscopy (EIS). Potentiodynamic measurements yielded a classical electrochemical passivation curve for both alkaline (KOH) and acidic (H_2SO_4) solution. In addition EIS-measurements were performed at several potentials in order to characterize the Nb/solution, and/or Nb/Nb_2O_5 / solution interfaces. The impedance behaviour of the passive films on Nb can be adequately described with a simple EEC; R_{el} in series with a parallel circuit CPE (Q) – $R_{ct(ox)}$. The calculate values of the passive oxide (Nb_2O_5) films resistivity ranged between 10^{11}–10^{10} Ω cm with relative dielectric constant ($\varepsilon_f \approx 14$) for KOH-solutions and approx. $2 \cdot 10^{12}$ Ω cm for 1M H_2SO_4, indicating that the Nb-passive films, generated in acidic solutions, are better corrosion protectors then those formed in alkaline solutions.

Key words: passive films; niobium; cyclic voltammetry; electrochemical impedance spectroscopy

ЕЛЕКТРОХЕМИСКА И ИМПЕДАНСНА КАРАКТЕРИЗАЦИЈА НА ПАСИВНИ ФИЛМОВИ НА НИОБИУМ ВО АЛКАЛНИ И КИСЕЛИ РАСТВОРИ

Електрохемиската карактеризација на анодните пасивни филмови формирани врз ниобиум во алкални (0,1 – 5 M KOH) и кисели раствори (H_2SO_4) е вршена со помош на циклична волтаметрија и електрохемиска импедансна спектроскопија (ЕИС). Со потенциодинамичките мерења се добиени класични електрохемиски пасивациски криви како во алкалните (KOH) така и во киселите раствори (H_2SO_4). Импеданските мерења беа изведени при неколку потенцијали за да се карактеризира граничната површина на Nb/раствор и/или Nb/Nb_2O_5/раствор. Импедансното однесување на пасивните филмови врз Nb може да се опише со едноставно еквивалентно електрично коло (ЕЕК); R_{el} сериски сврзан со паралелно коло CPE (Q) – $R_{ct(ox)}$. Пресметаните вредности на специфичните отпори ($10^{11} - 10^{10}$ Ω cm) и релативната диелектрична константа ($\varepsilon_f \approx 14$) на пасивните оксидни филмови во раствори на KOH и ~ $2 \cdot 10^{12}$ Ω cm за 1M H_2SO_4 укажуваат дека пасивните филмови на ниобиум создадени во кисели раствори имаат подобри корозивно-заштитни карактеристики од оние создадени во алкални раствори.

Клучни зборови: пасивни филмови; ниобиум; циклична волтаметрија; електрохемиска импедансна спектроскопија

INTRODUCTION

In recent years there has been a growing interest in niobium and its alloys for use in the chemical industry (construction of chemical plants), mechanical industry (construction of high pressure transmission pipelines) and the electrical industry (construction of super-conductive magnets). Nb has the highest transition temperature (9.3 K or – 264 °C) and among metals it is the most practical choice for super-conducting applications. Moreover, Nb possesses high corrosion resistance due to its ability to spontaneously form stable passive oxides in air and aqueous solutions. The thickness

of these films is 2–4 nm and it is extremely difficult to remove them from the metal surface. The corrosion resistance of Nb can be enhanced by electrochemical formation of passive and/or anodic oxide films on its surface [1–4]

The electrochemical passivity of Nb has been mainly studied using galvanostatic, potentiostatic, potentiodynamic and EIS techniques in weak acid and alkaline solutions, as well as neutral and puffer solutions [5–7].

Impedance data are diagnostically useful, as they can provide a variety of information, in particular on the main reactions contributing to the faradic current at the reacting interface, and on the electrical characteristics of the anodic films on the metal electrode [8–10].

The aim of this work was to investigate the electrical and corrosion properties of oxide films electrochemically grown in the initial stage of electrochemical passivation of Nb electrode, up to 1 V/she in aqueous KOH and H_2SO_4 solutions, using EIS. An attempt to characterize the Nb/electrolyte interface in the cathodic region, prior to the commencement of the passivation process, at – 0.2 V/she for 1M H_2SO_4 and –1 V/she for KOH solutions, was also made in this study.

EXPERIMENTAL

Annealed niobium rod (99.8 % purity; 6.35 mm diameter, Alfa Aesar-Johnson Mattey Company) in epoxy resin was used as a working electrode. Prior to each experiment, the electrode was mechanically polished with emery paper 600 and then electropolished at 15.2 V in bath consisting of 170 ml HNO_3 + 50 ml HF + 510 ml CH_3OH + 5 g citric acid. The counter electrode was a platinum wire and an Hg/HgO-electrode was used as a reference electrode. All the measured potentials are referred to the standard hydrogen electrode (she).

A classical three-compartment cylindrical electrolytic cell equipped with Luggin capillary and an inlet and outlet for bubbling inert gas was used. The solution in the cell was initially de-aerated by flowing nitrogen gas through a fritted bubbler for at least 30 min prior to the run.

Aqueous solutions of potassium hydroxide with concentrations of 0.1 M, 0.5 M, 1M, 2 M, 5 M KOH, and 1M sulfuric acid were prepared from KOH and concentrated H_2SO_4 (Merck, extra pure) with redistilled water ($k < 2 \cdot 10^{-7}$ Scm^{-1}). The

electrolyte in the cell was exchanged after each measurement, in order to avoid an eventual build up of soluble Nb species. The experiments were carried out at room temperature.

The EIS (electrochemical impedance spectroscopy) measurements were carried out in the frequency range from 100 kHz to 10 mHz (with a.c. signal of 5 mV) at several potentials: –1 V, 0.5 V and 1 V/she in the KOH solutions, and –0.2 V and 0.5 V/she in the H_2SO_4 solutions, in order to determine the characteristics of the Nb/solution and/or Nb-oxide/solution-interface. It should be mentioned that the Nb-electrode was treated for approx. 10 minutes at these specified potentials (–1 V; 0.5 V and 1 V/she and/or –0.2 V and 0.5 V/she) before every run of impedance measurement.

RESULT AND DISCUSSION

Cyclic voltammetry

The potentiodynamic measurements were performed after electrochemical treatment of the Nb-electrode (mechanically and electrochemically polished) at low cathodic potentials of –1 V/she for the KOH solutions and at –0.2 V/she for 1M H_2SO_4 for approx. 10 minutes.

In Fig. 1, potentiodynamic *I/E*-curves for first and second cycle of Nb electrode in 1M KOH (a) and 1M H_2SO_4 (b) are shown. The potential sweeps were performed in the potential window from –1.2 V/she to 4 V/she for 1 M KOH, and from – 0.2 V/she to 1.5 V/she for 1 M H_2SO_4, with sweep rate of 200 mV/s.

In the first positive scan three distinct regions for both potentiodynamic curves were observed.

The first region can be defined as an active dissolution region, where the anodic current increases exponentially with a scanning potential and an anodic current peak is formed. In this region the metal dissolution takes place following the reaction [11]:

$$Nb \rightarrow Nb^{5+} + 5e^-. \tag{1}$$
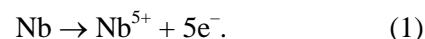
The second (passive) region corresponds to the electrochemical passivation of the Nb electrode following the reaction:
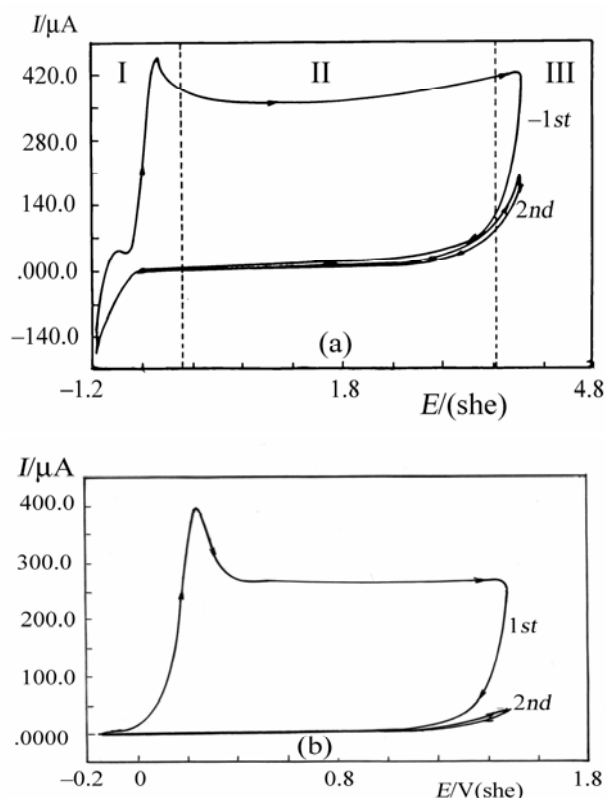
$$2Nb + 5H_2O \rightarrow Nb_2O_5 + 10H^+ + 10e^-. \tag{2}$$
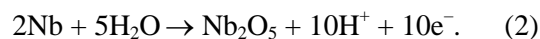
Fig. 1. Cyclic voltammograms of Nb electrode (0.316 cm²) recorded in 1 M KOH (a) and 1M H_2SO_4 (b); ($v = 200$ mVs⁻¹)

In this region, the anodic current is almost constant, independent of the applied potential, and a surface layer of stable oxides is formed. The thickness of the passive films grows by reaction (2) and the metal dissolution reaction (1) is increasingly hindered.

The progress of metal dissolution in the active region and passivation in the second region depends on the concentration of KOH and/or H_2SO_4, surface pre-treatments of the electrodes, and the initial electrochemical conditions.

The thickness of the passive films (L_f) was determined by the following equation:

$$L_f = q\, M_{Nb_2O_5}\, 10^7 / z\, F\, \rho_{Nb_2O_5}, \qquad (3)$$

where L_f is the film thickness (nm), q is the anodic charge (Ccm⁻²) (calculated from the area under the registered j/E-curves, region II, Fig. 1), M is the molecular weight of the passive film (in our case for Nb_2O_5, $M = 265.8$ gmol⁻¹), z is the number of electron exchanged (according to reaction 2 for Nb_2O_5 $z = 10$), ρ_{Nb2O5} is the density of a presumed homogeneous oxide ($\rho_{Nb_2O_5} = 4.47$ gcm⁻³) and F is the faradic constant (96 500 Cmol⁻¹).

It should be noted that the passivation current (nearly constant in this region-II) depends linearly on the sweep rate ($v = dE/dt$, Vs⁻¹) between 5 and 250 mVs⁻¹, with a slope (dj_{pass}/dv) ranging from 4.06 mCV⁻¹cm⁻² (or 2.5 nm/V) for H_2SO_4, to 5.68 mCV⁻¹cm⁻² (or 3.5 nm/V) for KOH solutions, assuming Nb_2O_5 as a passive film on the Nb surface. The calculated values of 2.5 nm/V (4·10⁶ V/cm) and/or 3.5 nm/V (5.6·10⁶ V/cm) indicate that the high field mechanism of ionic migration can be assumed for the process of electrochemical passivation of Nb. This statement is in a very good agreement with numerous literature data [12].

The third region is trans-passive where breakdown of the passive film and oxygen evolution takes place at potentials more anodic then 1.4 V/she for sulphuric acid, and more anodic then 3.6 V/she for KOH solutions (Fig. 1).

In the first reverse scans, up to potential of –1.2 V for 1 M KOH, and up to –0.2 V for 1 M H_2SO_4 (Fig. 1), no cathodic peaks or reactivation anodic peaks were observed. In the second cycles, constant currents close to zero for both forward and reverse scans were recorded. It is evident that after the first forward cycle the Nb electrode in 1 M H_2SO_4 and 1 M KOH remained passive in the whole investigated potential range, and the formed passive films blocked all possible redox reactions Nb/passive film/electrolyte at the interface.

Electrochemical impedance spectroscopy (EIS)

In order to characterize the Nb/solution and/ or Nb-oxide/solution-interfaces, the EIS measurements were carried out in the frequency range from 100 kHz to 10 mHz (with a.c. signal of 5 mV) at several potentials: –1 V (Nb/solution), 0.5 V and 1 V/she (Nb/Nb_2O_5/solution) in the KOH solutions, and at –0.2 V and 0.5 V/she in the H_2SO_4 solution. The obtained experimental results were fitted using the Boukamp program [13].

Analyzing the obtained Bode-plots (log$Z$/log$f$ and φ/log$f$) for impedance characterization of the Nb/KOH interface as a function of the potential (Fig. 2), as well as a function of KOH concentration (Fig. 3), the following can be concluded:

i) log$Z$/log$f$ and φ/log$f$ plots (Figs. 2 and 3) indicate the existence of mainly three regions. In the first one, at high frequencies (from 100 to 10 kHz), the measured impedances (Z) ranged be-

tween 2 and 40 Ω (or 0.63 – 12.6 Ω cm^2), with the phase angles from 0 to 10 degree, corresponding to the ohmic resistance of electrolyte (0.1 – 5 M KOH) between the working and the reference electrode.

ii) The second region, from ~ 10 kHz to 1 Hz (for 0.5 M and 1 M KOH); from 10 kHz to 10 Hz (for 2M KOH), and from 10 kHz to 100 Hz (for 5 M KOH), shows a linear log$Z$/log$f$ dependences with the slope: $\partial(\log Z)/\partial(\log f)$ ranged from –0.8 to –0.98 and phase angles between –50 and –88 degrees (non-ideal condenser). As far as this region is concerned, the impedance for non-ideal condenser (real metal-solution or passive film interface) can be represented as:

$$Z = 1/Q(j\omega)^n \qquad (4)$$

where $n < 1$ and for ideal condenser, $n = 1$ as:

$$Z = 1/C_{dl}(j\omega) \qquad (5)$$

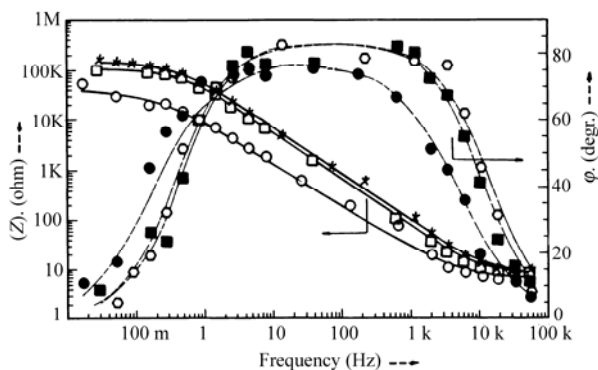where C_{dl} is a capacity of the electrochemical double layer.

Fig. 2. Bode-plots for impedance characterization of the Nb / 0.5 M KOH interface at: $E = –1$ V/she (–○–; –●–); $E = 0.5$ V/she (–□–; –■–); and $E = 1$V/she (–✱–; –◇–)
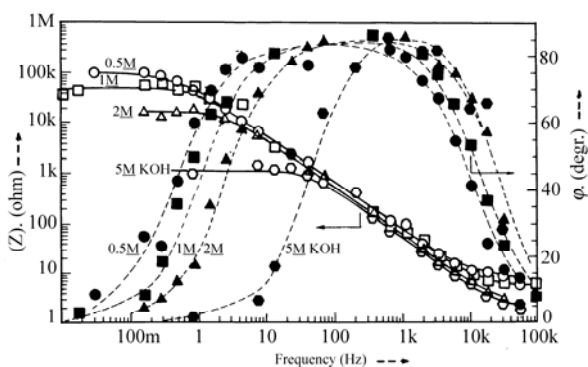

Fig. 3. Bode-plots for impedance characterization of the Nb/ Nb$_2$O$_5$/KOH interface at 0.5 V/she

The values obtained for the exponent *n* (between 0.8 and 0.98) indicate a relatively high homogeneity of the metal surface.

iii) At low frequencies (from 1 Hz to 10 mHz for 0.5 M and 1 M KOH, from 2 Hz to 200 mHz for 2 M KOH, and from 20 Hz to 1 Hz for 5 M KOH) the measured impendances (Z) (Fig. 3), are again practically insignificantly influenced by the frequency with a sharp decreases of the phase angle (from 30° to 0°). Thus the measured impedances in this region correspond to the sum of charge transfer resistance (R_{ct}) or oxide resistance (R_{ox}) and ohmic resistance of the electrolyte (R_{el}) ($Z = R_{ct(ox)} + R_{el}$).

The impedance behavior of the Nb/solution and/or Nb/oxide/solution-interfaces can be adequately described with a simple equivalent electric circuit ($R(QR)$), presented in Fig. 4.
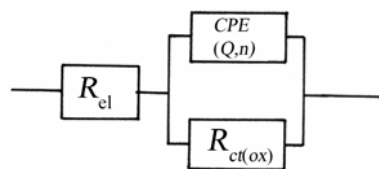

Fig. 4. Equivalent electric circuit for impedance characterization of Nb/solution and Nb/Nb$_2$O$_5$/solution-interface

The best fitting impedance parameters for the systems Nb/KOH or Nb/1 M H$_2$SO$_4$, were obtained for several electrode potentials and KOH concentrations using the experimentally obtained results and the Boukamp program [13]. These results are presented in Table 1.

These data indicate:

• The values of R_{el}, depends only on the KOH concentration, and decreases with increasing KOH concentration.

• The obtained values of Q (constant phase element – CPE; $C = Q^{1/n}$), Table 1, show that the double layer capacity of the Nb/KOH-interface at –1 V/she, ranged between 10 and 18 μFcm^{-2}, for Nb/Nb$_2$O$_5$/KOH at 0.5 V/she between 3.8 and 9.6 μFcm^{-2} or between 3.4 and 7.3 μFcm^{-2} at 1V/she, depending on the KOH concentration. The values of the capacities at 0.5 or 1 V/she are significantly lower compared to those at –1 V/she (without passive film), indicating the extension of the Helmholtz layer-thickness as a results of the passive film formation at the Nb/KOH-interface.

T a b l e 1

Best fitting parameters for systems: Nb/KOH; Nb/Nb$_2$O$_5$/KOH and Nb/1M H$_2$SO$_4$; Nb/ Nb$_2$O$_5$/1M H$_2$SO$_4$
using a simple R(QR) EEC (A$_{Nb}$ = 0.316 cm^2)

C$_{KOH}$/M	E/V(she)	R$_{el}$/Ω	Q/Ω^{-1}s^n	n	C/μFcm^{-2}	R$_{ct}$*(R$_{ox}$)/Ω
	−1.0	45.14	$7.0 \cdot 10^{-5}$	0.770	12.70	$4.43 \cdot 10^{4*}$
0.1	0.5	35.12	$3.67 \cdot 10^{-6}$	0.919	3.85	$9.70 \cdot 10^4$
	1.0	40.00	$3.73 \cdot 10^{-6}$	0.910	3.43	$6.65 \cdot 10^5$
	−1.0	6.50	$2.29 \cdot 10^{-5}$	0.845	10.20	$4.15 \cdot 10^{4*}$
0.5	0.5	7.98	$3.53 \cdot 10^{-6}$	0.939	4.94	$1.06 \cdot 10^5$
	1.0	8.14	$2.95 \cdot 10^{-6}$	0.932	3.70	$1.51 \cdot 10^5$
	−1.0	4.30	$5.47 \cdot 10^{-5}$	0.776	10.2	$6.80 \cdot 10^{4*}$
1.0	0.5	5.18	$3.30 \cdot 10^{-6}$	0.959	6.10	$5.05 \cdot 10^4$
	1.0	4.23	$3.22 \cdot 10^{-6}$	0.946	4.95	$4.90 \cdot 10^4$
	−1.0	2.21	$2.30 \cdot 10^{-5}$	0.863	13.45	$1.74 \cdot 10^{4*}$
2.0	0.5	2.30	$3.80 \cdot 10^{-6}$	0.963	7.45	$1.79 \cdot 10^4$
	1.0	2.44	$2.37 \cdot 10^{-6}$	0.976	5.45	$2.28 \cdot 10^4$
	−1.0	1.85	$1.72 \cdot 10^{-5}$	0.908	17.85	$0.95 \cdot 10^{3*}$
5.0	0.5	1.95	$3.04 \cdot 10^{-6}$	1.000	9.60	$1.12 \cdot 10^3$
	1.0	1.90	$3.00 \cdot 10^{-6}$	0.979	7.30	$3.41 \cdot 10^3$
1M H$_2$SO$_4$	−0.2	1.63	$3.89 \cdot 10^{-5}$	0.883	31.10	$2.41 \cdot 10^{3*}$
	0.5	1.75	$6.80 \cdot 10^{-6}$	0.954	12.10	$5.72 \cdot 10^5$

Thus, for Nb-electrode passivated at 1 V/she in 1 M KOH, the value of the relative dielectric constant of the passive film can be calculated using the data from Table 1 and the equation:

$$\varepsilon_{ox} = 1.13 \cdot L_{ox} \cdot C_{ox} = 1.13 \cdot 2.5 \cdot 5 \cong 14.1.$$

It should be noted that in this case, (Nb/Nb$_2$O$_5$/solution-interface), the capacity values will mainly depend on the characteristics and/or thickness of the passive film.

• The double layer capacity (*dlc*) of the Nb/solution interface at –1 V/she for KOH solutions, and –0.2 V/she for H$_2$SO$_4$ solution, is mainly determined by the adsorbed layer of the solvent (H$_2$O) molecules ($d_{H_2O} \approx 0.4$ nm) [14].

• The values of the charge transfer resistance (R_{ct}) and/or oxide resistance (R_{ox}) of the electrochemically formed passive films, Table 1, regularly depend on the electrode potential of passivation and KOH concentrations. For low concentrations of KOH (0.1 and 0.5 M) the value of R_{ox} for passive films formed at 0.5 V/she is approx. $1 \cdot 10^5 \Omega$ (or $3.2 \cdot 10^4 \Omega$ cm^2), for 1 M KOH R_{ox} is approx. $5 \cdot 10^4 \Omega$

(or $1.6 \cdot 10^4 \Omega$ cm^2), for 2 M KOH R_{ox} is approx. $1.8 \cdot 10^4 \Omega$ (or $5.7 \cdot 10^3 \Omega$ cm^2), and for 5 M KOH R_{ox} is approx. $1.12 \cdot 10^3 \Omega$ (or $3.54 \cdot 10^2 \Omega$ cm^2). The significant decrease of the oxide film resistance (for about two order of magnitude) at higher concentrations of KOH ($c_{KOH} \geq 1$ M), can be mainly attributed to the decreased chemical stability of the passive films. This statement was unambiguously confirmed during potentiodynamic measurements (dE/d$t < 5$ mVs^{-1}) of electrochemical passivation of Nb in KOH-solutions ($c_{KOH} \geq 5$ M) where the repassivation process can be almost completely repeated in the reverse scan [15].

• The calculated values of the Nb-oxide resistance at $E = 1$V/she and $L_{ox} \approx 3.5$ nm, using the equation:

$$\rho_{ox} = (R_{ox} \cdot A_{Nb}) / L_{ox} \, (\Omega \text{ cm}) \qquad (6)$$

and the presented data for R_{ox} for several KOH concentrations (Table 1), are as follows: $\rho_{ox} = 6 \cdot 10^{11}$ for 0.1 M KOH, $9.6 \cdot 10^{10}$ Ω cm for 0.5 M KOH, $4.4 \cdot 10^{10}$ Ω cm for 1M KOH, and $2.1 \cdot 10^{10}$ Ω cm for 2 M KOH.

These values indicate that the ohmic resistance (or conductivity) of the passive Nb-oxide films is strongly influenced by the KOH concentration.

• The same experimental and calculation procedure has also been applied for impedance characterization of the Nb/1 M H_2SO_4 at –0.2 V/she and Nb/Nb$_2$O$_5$/1 M H_2SO_4 at 0.5 V/she (Fig 5).
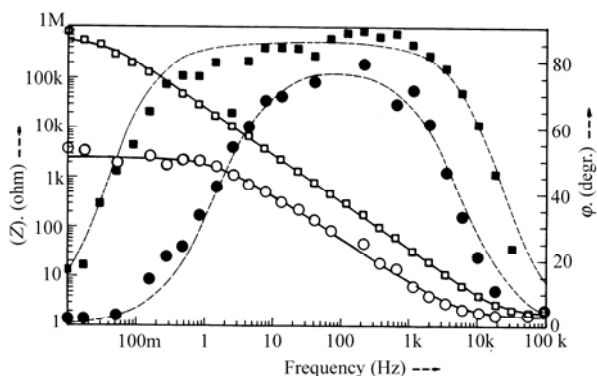
Fig. 5. Bode-plots for impedance characterization of the Nb / 1 M H_2SO_4 interface at E = –0.2 V/she (–○–; –●–) and Nb / Nb$_2$O$_5$ /1M H_2SO_4 at E = 0.5 V/she (–□– ; –■–)
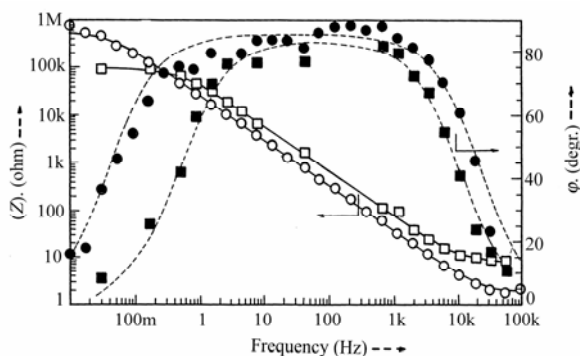
Fig. 6. Bode-plots for impedance characterization of the Nb / Nb$_2$O$_5$/0.5 M KOH (–□– ; –■–) and Nb / Nb$_2$O$_5$/1M H_2SO_4-interface (–o–; –●–) at E = 0.5 V/she

The calculated value of the oxide (Nb$_2$O$_5$) resistivity ($1.81·10^{12}$ Ω cm) in this case (1M H_2SO_4) (E = 0.5 V/she; $L_{ox} \approx$ 1.5 nm) indicates formation of a more compact and homogeneous protective film on the Nb-surface, as compared with that formed in 1M KOH, Fig. 6.

CONCLUSIONS

1) Potentiodynamic investigations of electrochemical passivation of Nb, both in aqueous solutions of KOH or H_2SO_4, indicate that the oxide-free Nb surface can be provided with cathodic treatment of the previously polished Nb-electrode (mechanically and electrochemically) in potentiostatic conditions, and potentials more cathodic then –0.9 V/she (in KOH solutions) or more cathodic then –0.15 V/she (in H_2SO_4 solutions).

2) The constant current for the process of electrochemical passivation of Nb in KOH solutions (j_{pass}), both for KOH and H_2SO_4 solution, linearly depends on the rate of polarization (V/s) with a slope of 5.7 and 4.1 mCV^{-1}cm^{-2} or 3.5 and 2.5 nmV^{-1}, respectively (assuming Nb$_2$O$_5$ passive layer at the Nb surface), usual value for electrochemical passivation of many other metals.

3) EIS experimental data clearly show that the double layer capacity of Nb/KOH-interface ranged between 10 and 18 μFcm^{-2} (at $E \approx$ –1 V/she); for Nb/Nb$_2$O$_5$/KOH between 3.8 and 9.6 μFcm^{-2} (at $E \approx$ 0.5 V/she) or between 3.4 and 7.3 μFcm^{-2} (at $E \approx$ 1V/she), depending on the KOH concentration.

It was also found that by increasing the KOH concentration over 1M (2 and 5 M KOH) the obtained passive films of Nb are not protective enough due to their decreased chemical stability (increasing values of the capacity and/or decreased values of the passive film resistivity).

4) The calculate values of the passive oxide (Nb$_2$O$_5$) films resistivity ranged between 10^{11} – 10^{10} Ωcm with relative dielectric constant ($\varepsilon_f \approx$ 14), for KOH solutions and approx. $2·10^{12}$ Ωcm for 1 M H_2SO_4 indicating that the Nb-passive films, generated in acidic solutions, are better corrosion protectors then those formed in alkaline solutions.

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