

Ionic and electronic conductivity of the surface film on titanium during pulse electrolysis of water

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The processes of corrosion and degradation of electrode materials are crucial for the efficiency of pulse electrolysis and are expected to depend on the electrical characteristics of the pulse (current/voltage, frequency, duty cycle). The aim of the present paper is to investigate the effect of these characteristics on the electrochemical properties of Ti electrodes. Pulse electrolysis was carried out in 6 M KOH for 24 and 72 h with current amplitude of 65 mA, frequencies of the signal of 0.5-10 kHz and pulse duty cycle between 1 and 99%. The electrochemical properties of the titanium anode and cathode surfaces after operation were characterized by electrochemical impedance spectroscopy in a borate buffer solution (pH 7.4) at the open circuit potential, as well as by linear sweep voltammetry in a similar solution containing an equimolar mixture of $K_4Fe(CN)_6$ and $K_3Fe(CN)_6$ as a redox couple to probe the electronic conductivity of the surface films.

Key words: pulse electrolysis, titanium, electrochemical impedance spectroscopy, linear sweep voltammetry, electronic and ionic conductivity.

INTRODUCTION

Pulse electrolysis of water is a highly efficient method of production of hydrogen/oxygen gas mixtures, sometimes called hydroxygen, that are successfully used as additives to hydrocarbon fuels in internal combustion engines [1-4]. The papers on pulse electrolysis of water to obtain hydrogen/oxygen mixtures are somewhat scarce [5-9], focusing on the effect of pulse regime on the overall process efficiency and the combustion properties of the respective gas mixtures. It was also demonstrated that application of short inductive voltage pulses to the cell allows the power of the primary circuit to be reduced, thereby reducing the total power necessary for electrolysis and achieving water splitting with an input voltage as low as 1 V [7,8]. The interpretation of the phenomena associated with hydroxygen production has been recently a cause of controversy, invoking a range of explanations from the formation of new forms of matter [10-12] to that of charged water gas clusters [13]. Regardless of the exact mechanism of the process, it seems well established that in conditions of pulse electrolysis of water, the rate of the process is increased in comparison to the dc regime. This poses more stringent requirements for the electrode materials since the processes of their corrosion and degradation are expected to depend

on the electrical characteristics of the pulse (current/voltage, frequency, duty cycle). In most of the commercial hydroxygen generators described thus far, austenitic stainless steels, as well as pure titanium were employed as both cathode and anode materials [14]. A search of the literature revealed a dearth of studies relevant to characterization and optimization of the electrode material with respect to its corrosion/degradation rates.

The aim of the present paper is to investigate the effect of pulse characteristics (duty cycle and frequency) on the electrochemical properties of commercially pure Ti under pulse electrolysis operating conditions and to correlate these properties with the surface state of the material. The electrochemical properties are characterized using both electrochemical impedance spectroscopy in an inert electrolyte and linear sweep voltammetry in a similar electrolyte containing a redox couple to probe the electronic conductivity of the surface film.

EXPERIMENTAL METHODS

The laboratory setup to study the effect of electrical characteristics of the pulse consisted of a home-designed high-power pulse generator (60 V/15 A), a dc power supply (BK Precision, 100 V/15 A), a 7-digit multimeter (Tektronix), a digital oscilloscope (Tektronix), and a flow meter (Aalborg, 240 L/h). The setup was originally designed for studies of the hydroxygen generation

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efficiency in larger electrolysis cells using current amplitudes up to 5 A. In the present paper, however, a smaller cell was used since the main goal was to investigate the degradation of the electrode material. Thus pulse electrolysis with current amplitudes of 12–250 mA, pulse frequencies (f) of 0.5 to 10 kHz and duty cycles (D) between 1 and 99% and a duration of 24 h was performed. The distance between the anode and the cathode in the pulse electrolysis cell was 1 cm.

Investigations were carried out on Grade 2 titanium (99.2%) that served both as an anode and cathode material. Its pretreatment consisted of mechanical abrasion with emery paper up to 2400 grade followed by rinsing with bi-distilled water. 6 M KOH prepared from a p.a. chemical and bi-distilled water was used as electrolyte.

The electrochemical properties of the electrodes after operation were characterized by electrochemical impedance spectroscopy in a borate buffer solution (0.5 M H_3BO_3 , 0.05 M $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, pH 7.4) at the open circuit potential, as well as by linear sweep voltammetry in a similar solution containing 0.5 M $\text{K}_4\text{Fe}(\text{CN})_6$ and 0.5 M $\text{K}_3\text{Fe}(\text{CN})_6$ (1:1) as a redox probe of the electronic conductivity of the surface films. Electrochemical measurements were performed with an Autolab PGSTAT30/FRA2 driven by GPES and FRA software (Eco Chemie). The sweep rate in voltammetric measurements was 1 mV s^{-1} , whereas the frequency range of the electrochemical impedance measurements was from 0.01 Hz to 50 kHz with an ac signal amplitude of 15 mV (rms). The linearity of the impedance spectra was checked by measuring at signal amplitudes from 5 to 15 mV, whereas their causality – by a Kramers-Kronig transform compatibility test embedded in the measurement software. Fitting of experimental voltammograms and impedance spectra to appropriate functions was performed using Originlab software.

RESULTS AND DISCUSSION

Electronic conductivity of the surface film

Results of the electrochemical probing of the electronic conductivity of surface films on cathodes and anodes after 24 h of operation with voltammetry in a borate buffer solution (pH 7.3) containing a $\text{K}_3\text{Fe}(\text{CN})_6/\text{K}_2\text{Fe}(\text{CN})_6$ redox couple are presented in Fig. 1 and Fig. 2, respectively. The curves were fitted to a Butler-Volmer equation describing a first-order electrochemical reaction limited by charge transfer, expressed as follows

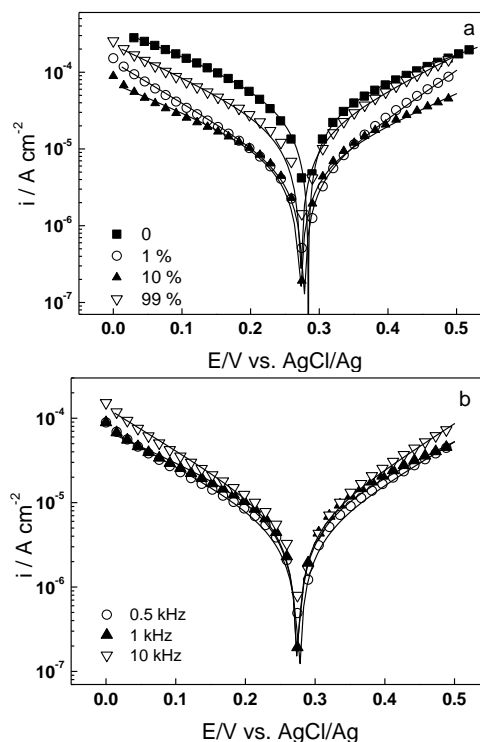


Fig. 1. Effect of pulse duty cycle (%) at constant frequency of 1 kHz (a) and frequency at a constant duty cycle of 10% (b) on the voltammetric response of Ti cathodes after 24 h of operation at 65 mA, measured in a borate buffer solution containing an equimolar mixture of $\text{K}_2\text{Fe}(\text{CN})_6$ and $\text{K}_3\text{Fe}(\text{CN})_6$. 0 – fresh sample. Points – experiment, lines – best-fit calculation.

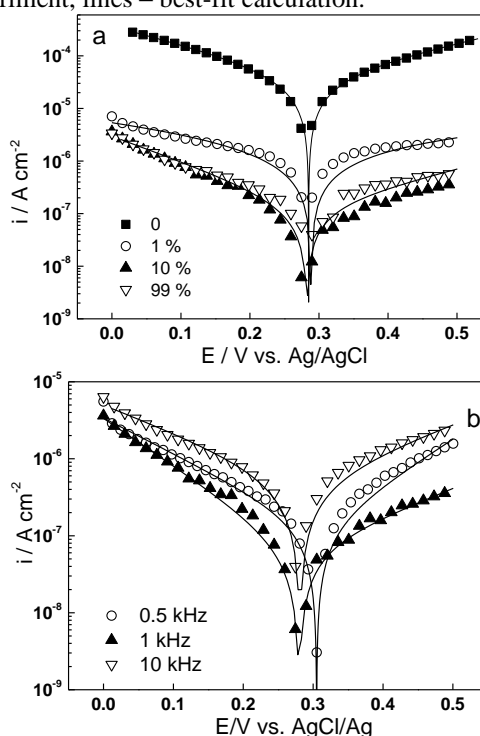


Fig. 2. Effect of pulse duty cycle (%) at constant frequency of 1 kHz (a) and frequency at a constant duty cycle of 10% (b) on the voltammetric response of Ti anodes after 24 h of operation at 65 mA, measured in a borate buffer solution containing an equimolar mixture of $\text{K}_2\text{Fe}(\text{CN})_6$ and $\text{K}_3\text{Fe}(\text{CN})_6$. 0 – fresh sample. Points – experiment, lines – best-fit calculation.

$$i = i_0 \left[\exp(b_a(E - E_{eq})) - \exp(-b_c(E - E_{eq})) \right] \quad (1)$$

where i_0 is the exchange current density of the redox reaction, b_a and b_c are the exponential coefficients and E_{eq} is the equilibrium potential of the redox couple (0.30 ± 0.02 V vs. AgCl/Ag). The best-fit calculations are shown in Fig. 1 and Fig. 2 with solid lines and demonstrate that this simple model describes adequately the experimental voltammograms.

In general, the electronic conductivity of the surface films formed on both anodes and cathodes, as characterized by the exchange current density, decreases with increasing the duty cycle at a constant frequency of 1 kHz (with the exception of 99% and dc regime) as well as with the increase of the pulse frequency at a duty cycle of 10% (Fig. 3).

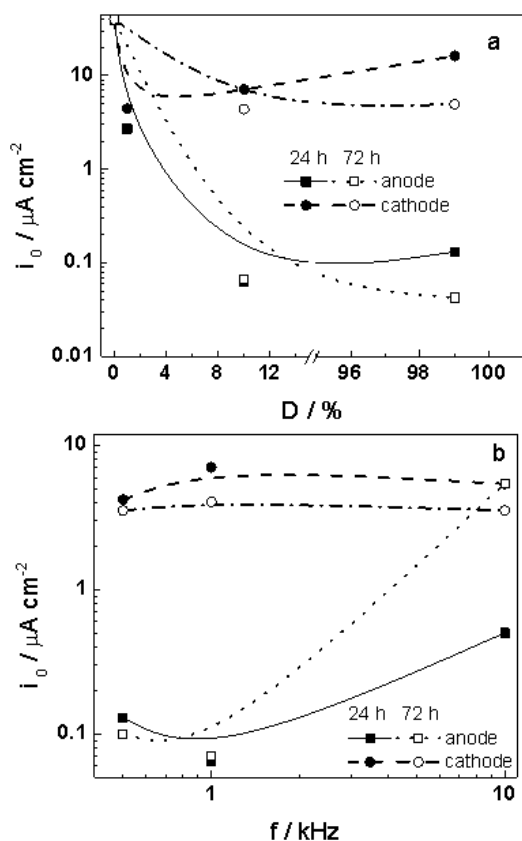


Fig. 3 A comparison between the exchange current density for Ti anode and cathode surfaces after 24 h and 72 h of operation at 65 mA/40 V for different duty cycles at a constant frequency of 1 kHz (a) and at different frequencies and a duty cycle of 10% (b).

However, this decrease is much more pronounced in the case of films formed on anodes and can be related to the increase of the thickness and/or decrease in the number of defects during the pulse anodic polarization. In that respect, it is worth

mentioning that the exponential coefficient of the oxidative partial reaction (b_a) is of the order of 6 V^{-1} , whereas that of the reductive partial reaction (b_c) is ca. 10 V^{-1} , i.e. the transfer coefficient for oxidation is smaller than that for reduction, as expected for an n-type semiconductor layer formed on the Ti surface during operation. The sum of the two exponential coefficients is however less than 40 V^{-1} which is expected for one-electron reaction at a bare metal surface. This fact is also in accordance that an oxide film is present on the surface and part of the applied potential is consumed as a potential drop in this oxide.

The superimposed effect of the increase of thickness (which lowers the probability for direct tunneling of carriers) and the decrease of the number of point defects (lowering the probability of resonance tunneling and/or polaron hopping) [15-17] qualitatively explains the influence of duty cycle on exchange current density (Fig. 3a). In the simplest case, when only direct tunneling is involved, the exchange current density should decrease exponentially with film thickness according to the equation

$$i_0 = i_{0,L_0} e^{-\beta(L-L_0)} \quad (2)$$

where i_{0,L_0} is the exchange current density of the fresh sample (bearing a native oxide with a thickness L_0), L is the thickness of the oxide on an electrode that has been in operation and β is the tunneling constant (of the order of 10^8 cm^{-1} [17,18]). The thickness of the native film on Ti being reported as 7.9 nm [19], the values of L estimated from equation (2) are of the order of 10-12 nm as depending on the duty cycle. These values demonstrate that during operation, film growth plays a minor role and most of the charge passed goes for water splitting.

Ionic conductivity of the surface films

Further insight into the influence of operational conditions on the electrochemical properties of the surface films on Ti was sought by registering electrochemical impedance spectra at open-circuit potential in a borate buffer solution (pH 7.3). The effect of the duty cycle at constant frequency of 1 kHz on the spectra is illustrated in Fig. 4 and Fig. 5 for the cathodes and anodes, respectively, after 24 h of service at current amplitude of 65 mA. Qualitatively similar spectra (not shown for the sake of brevity) were obtained as depending on the

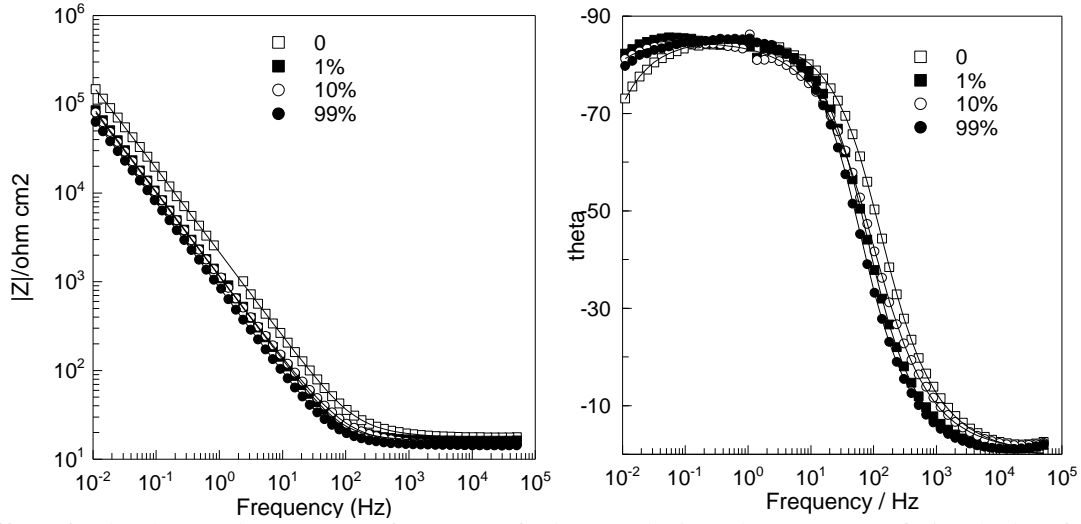


Fig. 4. Effect of pulse duty cycle at constant frequency of 1 kHz on the impedance spectra of Ti cathodes after 24 h of operation at 65 mA/40 V. Left- impedance magnitude vs. frequency, right – phase shift vs. frequency, 0 – fresh sample. Points – experiment, lines – best-fit calculation.

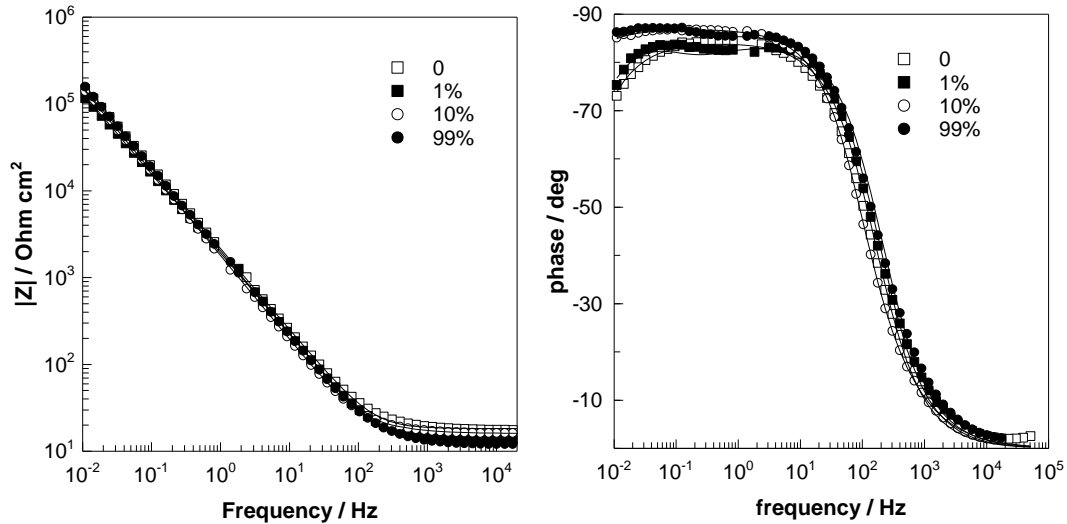


Fig. 5 Effect of pulse duty cycle at constant frequency of 1 kHz on the impedance spectra of Ti anodes after 24 h of operation at 65 mA/40 V. Left- impedance magnitude vs. frequency, right – phase shift vs. frequency, 0 – fresh sample. Points – experiment, lines – best-fit calculation.

pulse frequency at constant duty cycle. In the phase angle vs. frequency dependences, two overlapped time constants were detected by preliminary deconvolution of the impedance spectra. The higher frequency time constant is tentatively ascribed to the charge transfer processes at the film/solution interface, whereas the time constant at lower frequencies that is characterized by a much larger value of the associated resistance would correspond to the capacitance of the surface film in parallel to the resistance of ionic transport through it.

In order to extract quantitative information concerning the influence of pulse regime on the electrochemical properties of the surface films and their interface with the electrolyte, the impedance spectra were interpreted with the following transfer function

$$Z = R_{el} + \frac{1}{j\omega C_d + R_{ct}^{-1} + \frac{1}{j\omega C_f + R_{ion}^{-1}}} \quad (3)$$

where R_{el} is the uncompensated electrolyte resistance, C_d the interfacial double layer capacitance, R_{ct} – the charge transfer resistance at the film/solution interface, C_f – the capacitance of the semiconducting surface film and R_{ion} – the ionic transport resistance through the latter. It is worth mentioning that due to the geometrical and/or energetic non-homogeneity of the surface the capacitance of the double layer was approximated with a constant-phase element (CPE) and the values of the apparent capacitance were extracted from the data using the approach of Brug et al. [14]:

$$Q_{CPE}^{-1} = C_d^{1-\alpha} (R_{el}^{-1} + R_{ct}^{-1})^{\alpha} \quad (4)$$

where Q_{CPE} and α are the CPE parameters.

The best-fit calculations according to the above transfer function are presented in Fig. 4 - Fig. 5 with solid lines and demonstrate the adequacy of the model in describing the experimental data. It is worth mentioning that due to the significant overlap

of the two time constants, the values of the charge transfer resistance R_{ct} were computed with a large error and will not be commented further. Plots of the estimated values of the remaining transfer function parameters (C_d , R_{ion} and C_f) as depending on the operational characteristics of the pulse (duty cycle and frequency) for both anodes and cathodes that have been in service for 24 and 72 h at 65 mA are presented in Fig. 6 - Fig. 7.

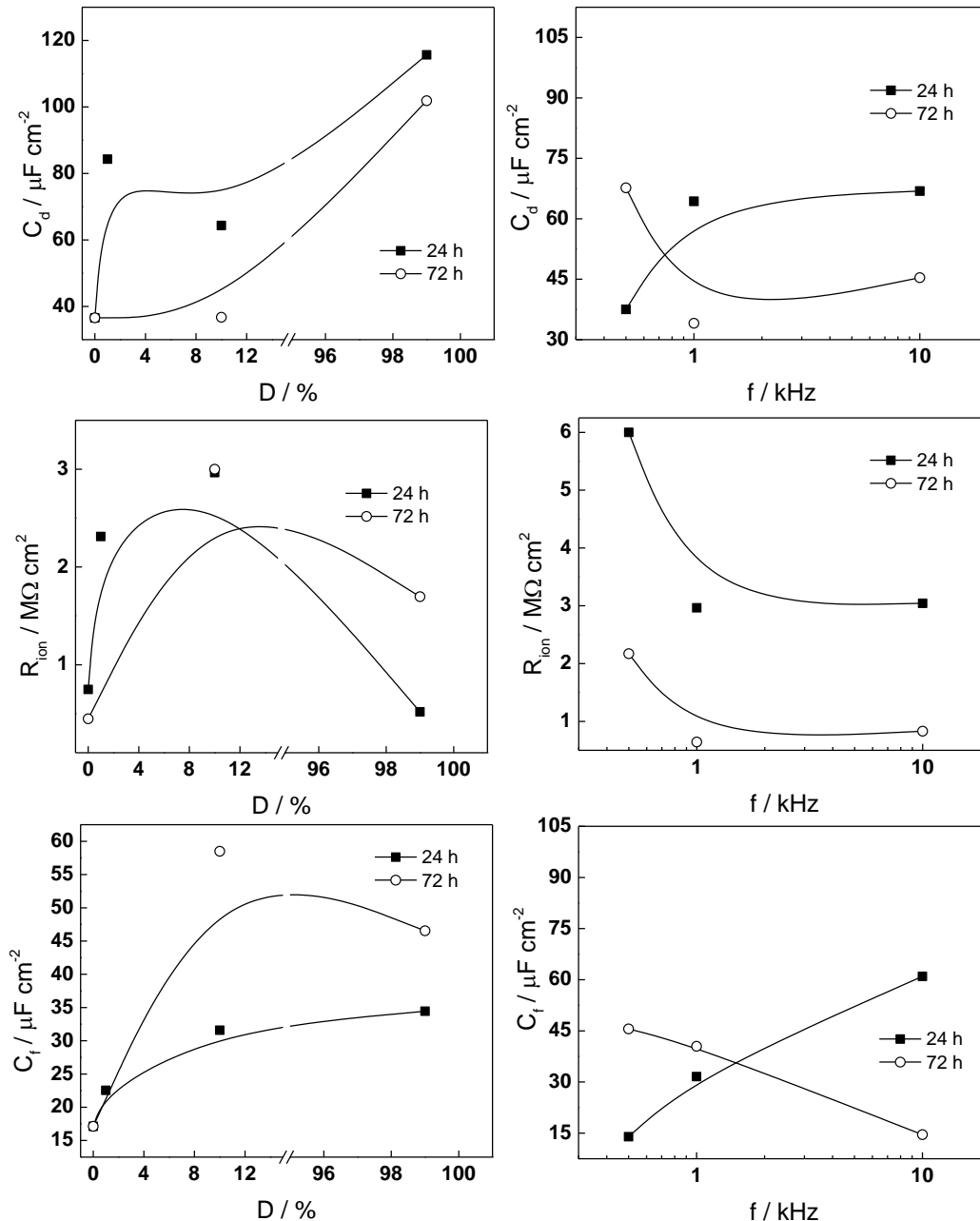


Fig. 6 A comparison between the double layer capacitance (above), the ionic transport resistance (middle) and the surface film capacitance (below) for Ti cathodes after 24 and 72 h of operation in a pulsed regime for different duty cycles at a constant frequency of 1 kHz (left) and for different frequencies at a duty cycle of 10% (right).

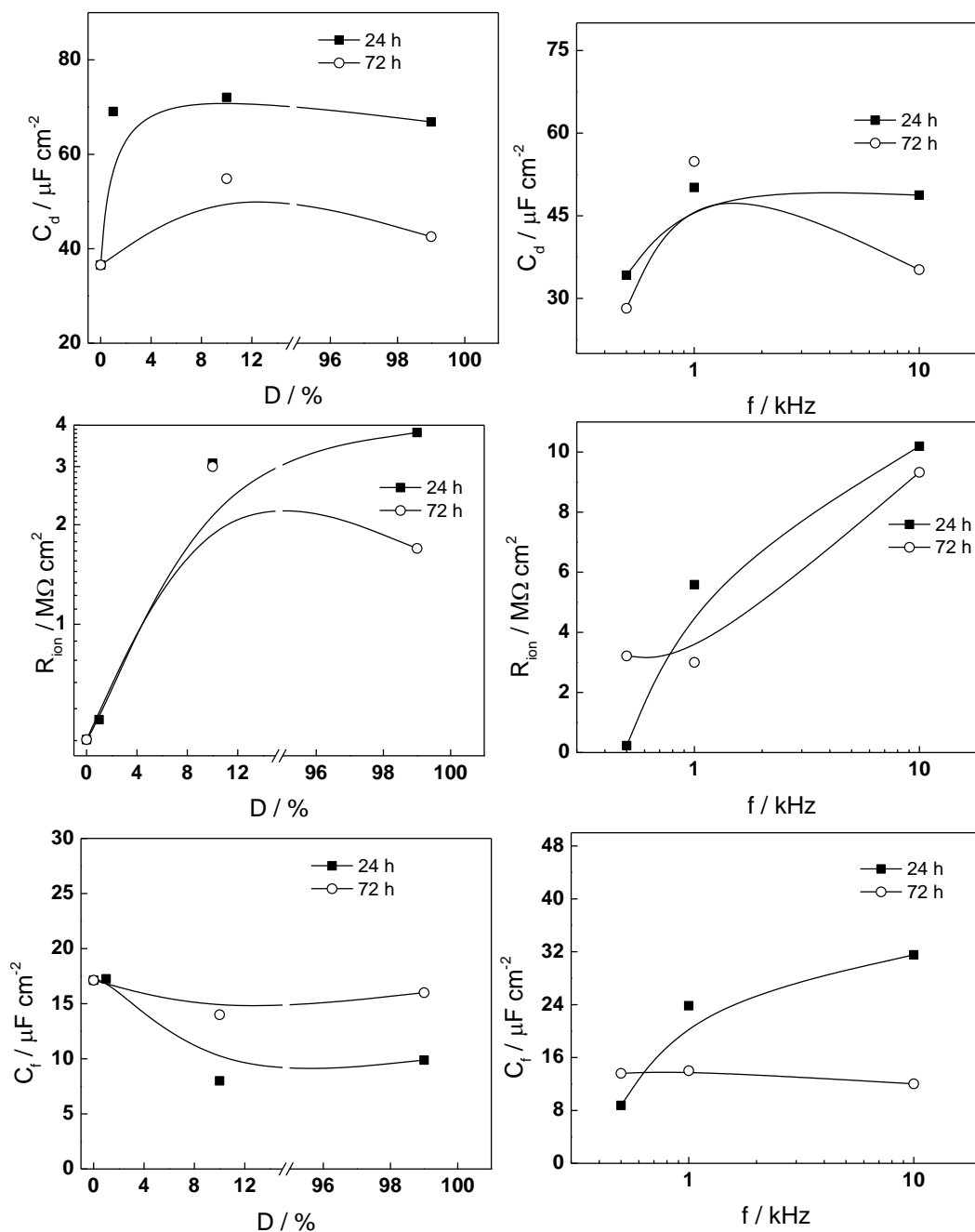


Fig. 7 A comparison between the double layer capacitance (above), the ionic transport resistance (middle) and the surface film capacitance (below) for Ti anodes after 24 and 72 h of operation in a pulsed regime for different duty cycles at a constant frequency of 1 kHz (left) and for different frequencies at a duty cycle of 10% (right).

The double layer capacitance increases with duty cycle, indicating an increase of the geometric and/or energetic heterogeneity of the surface as a result of pulse electrolysis operation. This increase is much more pronounced for the cathodes in accordance to what we reported in a parallel study of the effect of operational conditions on cathodes made of AISI 316L stainless steel [21].

The ionic conductivity of the oxide, that can be assumed to be inversely proportional to R_{ion} , decreases significantly for anodes in comparison to

a reference sample that has not been in operation. This trend can once more be correlated to oxide growth on the Ti surface during pulse electrolysis and/or decrease of the number of defects in the oxide. It is to a certain extent corroborated by the decrease of the film capacitance C_f , although the comparatively small decrease of this parameter indicates that it most probably represents the depletion layer in the semiconducting oxide, rather than being correlated to the whole thickness of the oxide.

If we assume that the oxidation reaction at open circuit is the growth of the oxide at the metal/film interface via inward high-field assisted migration of oxygen by a vacancy mechanism, balanced by chemical film dissolution at the oxide/solution interface, then the following approximate expression can be derived for the ionic transport resistance [22]

$$R_{ion} = \frac{RTa}{4F^2 D_o' (1-\alpha) k_g} k_c e^{L/a} \quad (5)$$

where a is the half-jump distance for ion transport, D_o' is the apparent (field-dependent) diffusion coefficient, α is the part of the applied potential consumed at the film/solution interface, k_g is the rate constant of generation of oxygen vacancies at the metal/film interface, k_c – the rate constant of consumption of the vacancies at the film/solution interface and L is the film thickness. According to this equation, the resistance of ionic transport is an exponential function of film thickness. Since it has been demonstrated above in relation to the effect of film thickness on the exchange current density of the redox reaction that film thickness increases with duty cycle, the exponential increase of R_{ion} with duty cycle that is detected in Fig. 7 can be understood in terms of equation (4). Of course, to quantify the effect of pulse parameters on film thickness and composition, surface analytical data are needed. In that context, further investigations of the composition of the oxide film with surface analytical techniques are underway in order to establish a quantitative correlation between surface layer composition and electrochemical properties.

CONCLUSION

The effect of dynamic characteristics of the process on the electrical and electrochemical properties of surface films formed on Grade 2 titanium during pulse electrolysis of alkaline solutions was characterized using voltammetry and electrochemical impedance spectroscopy. A conclusion can be drawn that the combination of electrochemical and surface analytical methods employed is suitable for the characterization of the electrochemical properties of electrode materials for pulse electrolysis of water. The decrease of the electronic conductivity of the anodes as a result of operation can be understood in terms of an increase of film thickness and hence a decrease of the probability of direct tunneling through the oxide as

the rate-controlling step of the redox reaction. The increase of film thickness, however, has been estimated to be relatively small and thus most of the charge passed is consumed for water splitting and formation of hydroxygen gas mixture. The ionic transport through the anodes has been qualitatively in terms of film growth via high-field assisted inward migration of oxygen by a vacancy mechanism. Further investigations using surface analytical techniques to obtain information on the composition and structure of the surface films would enable a quantitative correlation of these characteristics with the electrical and electrochemical properties of the oxides. Such studies are underway and the results will be reported in the near future.

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ЙОННА И ЕЛЕКТРОННА ПРОВОДИМОСТ НА ПОВЪРХНОСТНИ ФИЛМИ ВЪРХУ ТИТАН ПО ВРЕМЕ НА ИМПУЛСНА ЕЛЕКТРОЛИЗА НА ВОДА

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(Резюме)

Процесите на корозия и деградация на електродните материали са от решаващо значение за ефективността на импулсната електролиза и най-вероятно зависят от електричните характеристики на импулса (ток/напрежение, честота, наситеност на импулса). Целта на настоящата работа е да се изследва ефекта на тези характеристики върху електрохимичните свойства на титанови електроди. Импулсната електролиза е проведена в 6 М КОН за 24 и 72 часа с амплитуда на тока 65 mA, честоти на сигнала в интервала 0.5 – 10 kHz и наситеност на импулса между 1 и 99 %. Електрохимичните свойства на повърхностите на титановите аноди и катоди след електролиза са изследвани чрез електрохимична импедансна спектроскопия в разтвор на боратен буфер (pH 7.4) при потенциал на отворена верига, а също така и с линейна волтаметрия в подобен разтвор, съдържащ еквинормална смес от $K_4Fe(CN)_6$ и $K_3Fe(CN)_6$ като редокс двойка с цел изследване на електронната проводимост на повърхностните филми.