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Differences in the electrochemical behavior of ruthenium and iridium oxide in electrocatalytic coatings of activated titanium anodes prepared by the sol–gel procedure

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Abstract: The electrochemical characteristics of $Ti_{0.6}Ir_{0.4}O_2/Ti$ and $Ti_{0.6}Ru_{0.4}O_2/Ti$ anodes prepared by the sol–gel procedure from the corresponding oxide sols, obtained by force hydrolysis of the corresponding metal chlorides, were compared. The voltammetric properties in H_2SO_4 solution indicate that $Ti_{0.6}Ir_{0.4}O_2/Ti$ has more pronounced pseudocapacitive characteristics, caused by proton-assisted, solid state surface redox transitions of the oxide. At potentials negative to $0.0\ V_{SCE}$, this electrode is of poor conductivity and activity, while the voltammetric behavior of the $Ti_{0.6}Ru_{0.4}O_2/Ti$ electrode is governed by proton injection/ejection into the oxide structure. The $Ti_{0.6}Ir_{0.4}O_2/Ti$ electrode had a higher electrocatalytical activity for oxygen evolution, while the investigated anodes were of similar activity for chlorine evolution. The potential dependence of the impedance characteristics showed that the $Ti_{0.6}Ru_{0.4}O_2/Ti$ electrode behaved like a capacitor over a wider potential range than the $Ti_{0.6}Ir_{0.4}O_2/Ti$ electrode, with fully-developed pseudocapacitive properties at potentials positive to $0.60\ V_{SCE}$. However, the impedance characteristics of the $Ti_{0.6}Ir_{0.4}O_2/Ti$ electrode changed with increasing potential from resistor-like to capacitor-like behavior.

Keywords: activated titanium anodes; sol–gel procedure, ruthenium and iridium oxide; electrochemical impedance spectroscopy; pseudocapacitance.

INTRODUCTION

Titanium anodes coated with noble metal oxides (activated titanium anodes, ATA), being electrocatalytically active for the chlorine evolution and oxygen re-

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action,[1] are commercially applied in industrial electrochemistry for chlor–alkali electrolysis, cathodic protection and metal electrowinning processes.[2] ATA coatings with RuO_2 and/or IrO_2 undergo degradation due to the electrochemical dissolution of noble metal oxide species.[3–6] Since these products of noble metal oxide degradation are soluble, the anode coating is gradually enriched in insulating TiO_2 during operation, since not only is this oxide already present as a stabilizing component of binary and/or ternary coatings, but it also comes from the coating substrate. These processes lead to anode passivation.[3–5]

The anode activity for the oxygen evolution reaction plays a key role in the process of anode degradation.[5,6] It is known that ATA with iridium oxide in the coating is more stable against passivation in the electrolysis of NaCl solutions than a binary RuO_2–TiO_2 coating.[7,8] This is due to the slower dissolution rate of IrO_2 with respect to RuO_2, especially when a considerable portion of the current is related to the oxygen evolution reaction. For this reason, commercially available ATAs contain iridium oxide in small amounts, in addition to ruthenium and titanium oxide. A recent investigation showed that a RuO_2–IrO_2–TiO_2 anode is an ideal anti-fouling electrode material in the electrolysis process of brine.[9]

Previous studies[6,10,11] postulated a higher activity for the chlorine and oxygen evolution reaction, as well as greater stability to passivation of $Ti_{0.6}Ru_{0.4}O_2$ coatings on titanium prepared by the sol-gel procedure in comparison to the same coating prepared by the usual thermal decomposition of metal chlorides.[5,11] This improvement was assigned to the larger real surface area of the sol–gel-prepared coating.[6]

The activity and stability of a ternary $Ti_{0.6}Ru_{0.3}Ir_{0.1}O_2$ coating on titanium prepared by the sol–gel procedure were investigated under conditions of chlorine and oxygen evolution.[12,13] The anode characteristics were compared to the characteristics of a binary $Ti_{0.6}Ru_{0.4}O_2$ coating. The investigation showed that finely dispersed iridium oxide was produced by the sol–gel procedure.[13] It was found by an accelerated stability test in sea water that the ternary coating was considerably more stable during exploitation than the binary one.[12] This was assigned to the greater stability of nano-sized IrO_2 under vigorous oxygen and chlorine evolution in comparison to sol–gel processed RuO_2.

The aim of this study was to investigate the differences in electrochemical properties of $Ti_{0.6}Ir_{0.4}O_2$/Ti and $Ti_{0.6}Ru_{0.4}O_2$/Ti anodes prepared by the sol–gel procedure, in order to obtain further insight into the differences between the noble oxides, which result in the beneficial behavior of IrO_2-containing coatings.

EXPERIMENTAL

Colloidal dispersions of ruthenium, iridium and titanium oxide were obtained by the forced hydrolysis of the corresponding metal chlorides in boiling 0.27 mol dm^{-3} HCl.[11,13] The dispersions of RuO_2, IrO_2 and TiO_2 (oxide sols) were formed during 46, 20 and 10 h (ageing times), respectively. These ageing times were chosen since $Ti_{0.6}Ru_{0.4}O_2$ coatings with the best

electrochemical properties were obtained from sols of these ageing times,[9] while the ageing time of IrO_2 was set in-between. The prepared oxide sols were mixed to form binary dispersions for the preparation of a coating with the desired compositions of $Ti_{0.6}Ir_{0.4}O_2$ and $Ti_{0.6}Ru_{0.4}O_2$. The dispersions were painted over Ti plates (1 cm×1 cm×0.89 mm), previously sand-blasted, degreased in saturated NaOH/ethanol solution and etched in hot 20 mass % HCl for 20 min. The coatings were applied in two layers, each converted into the gel phase at 90 °C and annealed at 450 °C; the first layer was annealed for 10 min and the second for 20 min. This procedure developed the crystal structure of the oxide and provided good coating adhesion. The total coating mass was 1.0 mg cm^{-2} (calculated to the overall oxide).

The capacitive behavior of the prepared anodes was investigated by cyclic voltammetry (CV) in 1.0 mol dm^{-3} H_2SO_4 and by electrochemical impedance spectroscopy (EIS) in the same solution at the characteristic potentials indicated by the CV behavior of the prepared anodes. The polarization characteristics of the prepared oxide coatings in 1.0 mol dm^{-3} H_2SO_4 and in 0.50 mol dm^{-3} NaCl, pH 2, were registered by anodic linear sweep voltammetry at a scan rate of 0.50 mV s^{-1}. A Pt plate electrode was used as the counter electrode, while the reference electrode was a SCE, and all potentials are referred to the SCE.

RESULTS AND DISCUSSION

Colloidal dispersions of ruthenium, iridium and titanium oxide of different degrees of polydispersity were obtained.[13] The TiO_2 sol consisted of particles of size around 100 nm with a weak tendency to agglomerate. The RuO_2 particle size fell in the range 3–10 nm; however, the sporadic presence of agglomerates of sizes of several hundreds of nm was also evidenced.[13] The agglomeration was more pronounced upon dilution due to the increase in pH of the dispersion. A high affinity for agglomeration was also registered in the case of the IrO_2 particles, which were prepared as ultra-small (around 1 nm)[13] but, upon dilution, the stable iridium oxide agglomerates had sizes of 50–90 nm.

The capacitive cyclic voltammograms of $Ti_{0.6}Ir_{0.4}O_2$/Ti and $Ti_{0.6}Ru_{0.4}O_2$/Ti electrodes in H_2SO_4 solution, registered at different sweep rates, are shown in Figs. 1A and 1B, respectively. The voltammograms for the different coatings are of different shape, with much more pronounced pseudocapacitive reversible peaks for the $Ti_{0.6}Ir_{0.4}O_2$/Ti electrode, which are to be ascribed to proton-assisted, solid state surface redox transitions (SSRTs) of the noble metals (Me):[1,11,14]

$$MeO_x(OH)_y + \delta H^+ + \delta e^- \rightarrow MeO_{x-\delta}(OH)_{y+\delta}, \ 0 \leq \delta \leq 2 \qquad (1)$$
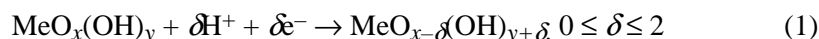
In the case of the $Ti_{0.6}Ru_{0.4}O_2$/Ti electrode (Fig. 1B), the SSRTs are over-lapped in the investigated potential range and form a single broad peak around 0.55 V, while at least three well-resolved SSRTs are seen for $Ti_{0.6}Ir_{0.4}O_2$/Ti as peaks at 0.35, 0.74 and 1.02 V (Fig. 1A, 50 mV s^{-1}). The most negative and positive peaks showed appreciable dependence on the sweep rate; the first one diminishes and the last one shifts cathodically with increasing sweep rate, and finally (at 300 mV s^{-1}) emerges with an SSRT peak at 0.74 V. In addition to the better separation of the SSRTs in the case of $Ti_{0.6}Ir_{0.4}O_2$/Ti, the associated capacitance values were much higher than for $Ti_{0.6}Ru_{0.4}O_2$/Ti.
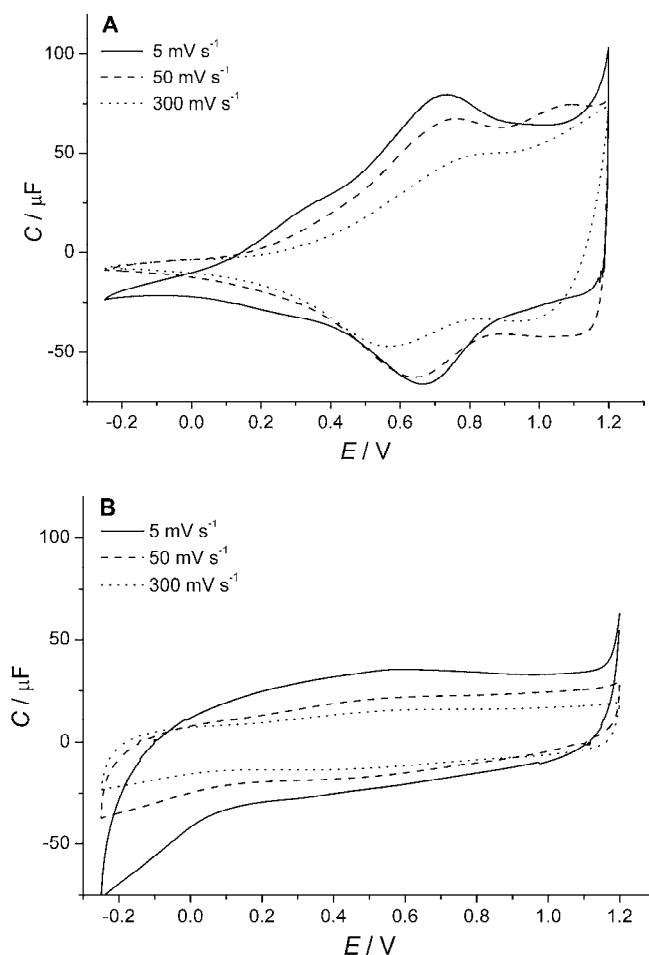
Fig. 1. Capacitance–potential curves of the $Ti_{0.6}Ir_{0.4}O_2$/Ti (A) and $Ti_{0.6}Ru_{0.4}O_2$/Ti (B) electrodes registered in 1.0 mol dm^{-3} H_2SO_4 at the sweep rates shown in the graph; room temperature.

The most remarkable difference in the CV behavior of the investigated electrodes is seen in the potential region below 0.0 V. The capacitance of $Ti_{0.6}Ir_{0.4}O_2$//Ti considerably decreases, which indicates poor conductivity in the cathodic direction, while $Ti_{0.6}Ru_{0.4}O_2$/Ti exhibits a considerable increase in the cathodic capacitance, due to pronounced proton injection according to Eq. (1). Hence, the data shown in Fig. 1 introduce iridium oxide as good anodic capacitor, while ruthenium oxide has desirable capacitive properties at more negative potentials.

The polarization curves of $Ti_{0.6}Ir_{0.4}O_2$/Ti and $Ti_{0.6}Ru_{0.4}O_2$/Ti anode in oxygen and chlorine evolution are shown in Fig. 2. The anodes showed different Tafel slopes for O_2 evolution (40 and 60 mV dec^{-1}, for the $Ti_{0.6}Ir_{0.4}O_2$/Ti and

$Ti_{0.6}Ru_{0.4}O_2$/Ti anodes, respectively), which promotes iridium oxide as a much better catalyst for this reaction. Only below 1.25 V were higher currents registered for the $Ti_{0.6}Ru_{0.4}O_2$/Ti anode. In the case of Cl_2 evolution, a slope close to 40 mV was registered for both anodes. The currents were higher for the $Ti_{0.6}Ru_{0.4}O_2$/Ti anode up to a potential close to the onset of O_2 evolution (near 1.15 V). These data show that the anode containing iridium oxide should behave beneficially from the standpoint of anode stability, as was already evidenced by comparison of $Ti_{0.6}Ru_{0.3}Ir_{0.1}O_2$/Ti and $Ti_{0.6}Ru_{0.4}O_2$/Ti anodes during their operation in sea water.[12]
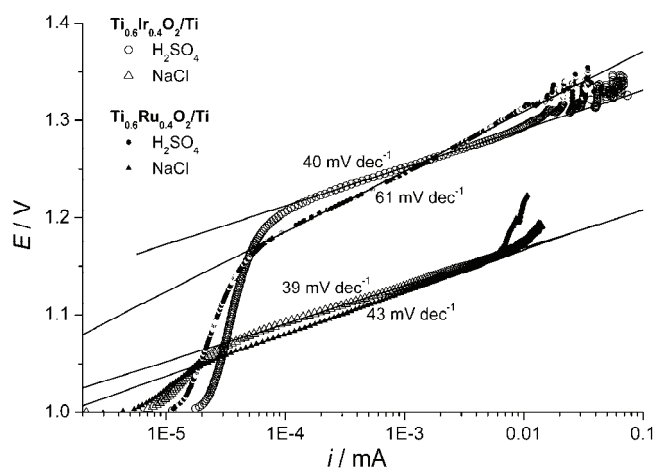

Fig. 2. Polarization curves of the $Ti_{0.6}Ir_{0.4}O_2$/Ti and $Ti_{0.6}Ru_{0.4}O_2$/Ti anodes registered in 1.0 mol dm^{-3} H_2SO_4 and in 0.50 mol dm^{-3} NaCl, pH 2; room temperature.

The EIS characteristics of $Ti_{0.6}Ir_{0.4}O_2$/Ti and $Ti_{0.6}Ru_{0.4}O_2$/Ti electrodes, registered at the characteristic potentials (–0.10, 0.35 and 0.74 V) related to CV behavior of the $Ti_{0.6}Ir_{0.4}O_2$/Ti electrode (Fig. 1A), are shown in Figs. 3 and 4, respectively.

The EIS data for the $Ti_{0.6}Ru_{0.4}O_2$/Ti electrode showed a much less pronounced dependence on potential (Fig. 4) than the $Ti_{0.6}Ru_{0.4}O_2$/Ti electrode. At all investigated potentials, the former electrode behaved like a capacitor and the changes of the EIS characteristics with potential were registered in the low frequency region (below 1 Hz). A low frequency capacitive loop clearly developed at 0.74 V, while at lower potentials the low frequency data indicate diffusion limitations. Since SSRTs dominate in the capacitive behavior of ruthenium oxide at the potentials positive to 0.60 V (Fig. 2B), it can be concluded that the low frequency capacitive loop at 0.74 V corresponds to a fully-developed pseudocapacitive behavior caused by SSRTs. At lower potentials, the SSRTs are controlled by proton injection/ejection through the porous structure of the coating.
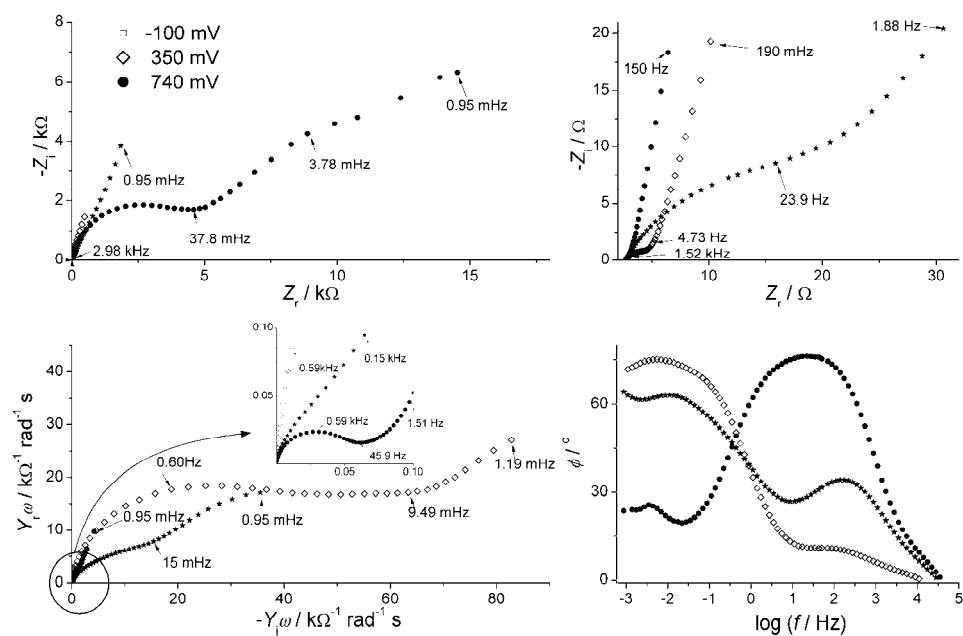
Fig. 3. The EIS characteristics of the $Ti_{0.6}Ir_{0.4}O_2/Ti$ electrode registered at different potentials in 1.0 mol dm^{-3} H_2SO_4 at room temperature.
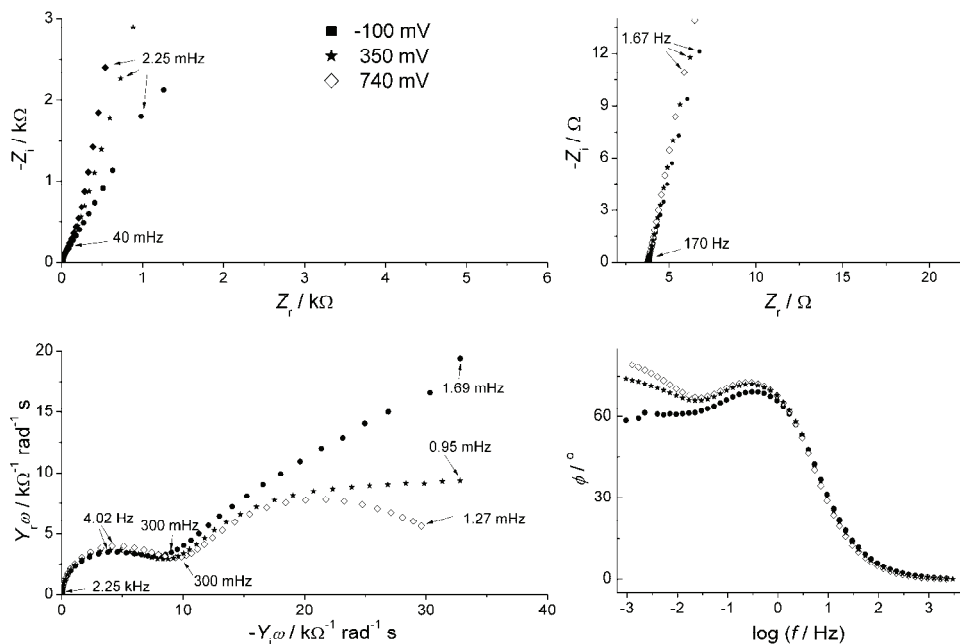

Fig. 4. The EIS characteristics of the $Ti_{0.6}Ru_{0.4}O_2/Ti$ electrode registered at different potentials in 1.0 mol dm^{-3} H_2SO_4 at room temperature.

The $Ti_{0.6}Ir_{0.4}O_2/Ti$ electrode behaved much like a resistor at –0.10 V (Fig. 3), as is indicated by the appearance of a semicircle in the complex plane plot, which corresponds to a considerably lower capacitance in comparison to the $Ti_{0.6}Ru_{0.4}O_2/Ti$ electrode (also registered by CV measurements, Fig. 1). As the potential increases, SSRTs are involved and the semicircle diminishes (the associated resistance decreases from $\approx$ 5 kΩ (–0.10 V) to $\approx$ 5 Ω (0.74 V)). At 0.74 V, a capacitive loop clearly developed and the electrode behaved much like capacitor upon the onset of SSRTs. The associated capacitance is much higher in comparison to that of the $Ti_{0.6}Ru_{0.4}O_2/Ti$ electrode, as was also indicated by CV measurements (Fig. 1).

CONCLUSIONS

The electrochemical properties of $Ti_{0.6}Ir_{0.4}O_2/Ti$ and $Ti_{0.6}Ru_{0.4}O_2/Ti$ anodes were investigated and compared, in order to obtain further insight into the differences between the two noble metal oxides, whereby iridium oxide was shown to be more stable in electrolysis processes involving simultaneous oxygen evolution. Cyclic voltammetry and electrochemical impedance spectroscopy showed that the $Ti_{0.6}Ir_{0.4}O_2/Ti$ electrode changed its behavior with the potential from resistor-like to capacitor-like due to the suppression of the proton injection/ejection process (resistor-like behavior). The $Ti_{0.6}Ru_{0.4}O_2/Ti$ electrode behaved as capacitor over the whole potential window of water stability. Proton-assisted, solid state surface redox transition processes, responsible for the pseudocapacitive behavior of noble oxides, were more pronounced in the case of the iridium oxide-containing electrode. Additionally, the $Ti_{0.6}Ir_{0.4}O_2/Ti$ anode was more active for oxygen evolution and of similar activity for chlorine evolution in comparison to the $Ti_{0.6}Ru_{0.4}O_2/Ti$ anode. It appears that the higher activity for oxygen evolution and greater stability of the $Ti_{0.6}Ir_{0.4}O_2/Ti$ anode are closely connected to the much better resolved redox transition process of iridium oxide. The state of the oxide formed prior to the oxygen evolution is more stable and active than the appropriate state of ruthenium oxide.

И З В О Д

РАЗЛИКЕ У ЕЛЕКТРОХЕМИЈСКОМ ПОНАШАЊУ ОКСИДА РУТЕНИЈУМА И ИРИДИЈУМА У ЕЛЕКТРОКАТАЛИТИЧКИМ ПРЕВЛАКАМА АКТИВИРАНИХ ТИТАНСКИХ АНОДА ДОБИЈЕНИХ СОЛ–ГЕЛ ПОСТУПКОМ

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У раду су испитиване електрохемијске карактеристике $Ti_{0.6}Ir_{0.4}O_2/Ti$ и $Ti_{0.6}Ru_{0.4}O_2/Ti$ анода добијених сол–гел поступком из оксидних солова синтетисаних форсираном хидроли-

зом одговарајућих хлорида метала. Волтаметријске карактеристике у раствору H_2SO_4 указују на више изражено псеудокапацитивно понашање $Ti_{0,6}Ir_{0,4}O_2$/Ti електроде које је последица површинских редокс прелаза у чврстом стању уз учешће протона. На потенцијалима негативнијим од 0,0 V_{ZKE} ова електрода показује слабу проводност и активност, док волтаметријским понашањем $Ti_{0,6}Ru_{0,4}O_2$/Ti електроде доминира продор протона у структуру оксида. $Ti_{0,6}Ir_{0,4}O_2$/Ti анода је електрокаталитички активнија за реакцију издвајања кисеоника, док су аноде сличних активности за реакцију издвајања хлора. Импедансне карактеристике формираних анода показују да се $Ti_{0,6}Ru_{0,4}O_2$/Ti електрода понаша слично кондензатору у ширем опегу потенцијала него што је то случај са $Ti_{0,6}Ir_{0,4}O_2$/Ti електродом, са потпуно развијеним псеудокапацитивним својствима на потенцијалима позитивнијим од 0,60 V_{ZKE}. С друге стране, за $Ti_{0,6}Ir_{0,4}O_2$/Ti електроду се уочава прелаз са карактеристика сличних отпорнику на карактеристике сличне кондензатору са порастом потенцијала електроде.

REFERENCES

1. S. Trasatti, in *Interfacial Electrochemistry – Theory, Experiment and Applications*, A. Wieckowski, Ed., Marcel Dekker Inc., New York, 1999, p. 769
2. De Nora elettrodi network, http://www.denora.com/Products/tabid/66/Default.aspx (February, 2009)
3. F. Beck, *Electrochim. Acta* **34** (1992) 811
4. L. M. Gajić-Krstajić, T. L. Trišović, N. V. Krstajić, *Corr. Sci.* **46** (2004) 65
5. V. Jovanović, A. Dekanski, P. Despotov, B. Nikolić, R. Atanasoski, *J. Electroanal. Chem.* **339** (1992) 147
6. V. Panić, A. Dekanski, V. B. Mišković–Stanković, S. Milonjić, B. Nikolić, *J. Electroanal. Chem.* **579** (2005) 67
7. V. V. Gorodetskii, V. A. Neburchilov, V. I. Alyab'eva, *Russ. J. Electrochem.* **41** (2005) 1111
8. T.-X. Cai, H. Chen, H. Ju, L.-N. Lu, *Corr. Prot.* **27** (2006) 522
9. C. Liang, N. Huanga, *Mater. Chem. Phys.* **111** (2008) 244–248
10. V. Panić, A. Dekanski, S. Milonjić, R. Atanasoski, B. Nikolić, *Electrochim. Acta* **46** (2000) 415
11. V. V. Panić, B. Ž. Nikolić, *J. Serb. Chem. Soc.* **73** (2008) 1083
12. V. V. Panić, B. Ž. Nikolić, *J. Serb. Chem. Soc.* **72** (2007) 1393
13. V. V. Panić, A. B. Dekanski, M. Mitrić, S. K. Milonjić, V. B. Mišković-Stanković, B. Ž. Nikolić, *Phys. Chem. Chem. Phys.* **12** (2010) 7521
14. V. V. Panić, *J. Serb. Chem. Soc.* **73** (2008) 661.