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ELECTROCHEMICAL BEHAVIOUR OF METALLIC TITANIUM IN MnO_2 ELECTROSYNTHESIS FROM SYNTHETIC SOLUTIONS SIMULATING SPENT BATTERY LEACH LIQUORS

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ABSTRACT. Electrochemical power cells with MnO_2 cathode represent an important waste group. After discharge, trough leaching and anodic electrosynthesis, this oxide can be recovered. Pure titanium represents an interesting substrate for this process both economically and environmentally.

In H_2SO_4 electrolytes titanium exhibits active corrosion, active–passive transition and passive voltage regions. At higher polarization, dielectric breakdown of the passive layer occurs, resulting in oxygen evolution. In the presence of Mn^{2+} ions the titanium active corrosion is inhibited and at higher potentials oxidation of the manganese ions occurs. Anodic surface modification by potentiostatic sweeping is proposed in presence of Mn^{2+} ions. During MnO_2 electrosynthesis tests on the modified electrode, no passivation was observed, which is not in agreement with the literature. Our measurements prove the feasibility of titanium usage as an anode in the electrolytic recovery route of MnO_2 from spent household Zn-Mn battery leach liquors.

***Keywords**: titanium; corrosion; passivation; EMD; spent battery leach liquors*

INTRODUCTION

Latest European Environmental Agency's waste management indicators show, despite existing regulations, that waste quantity generated per capita did not drop in the last 11 years and might increase in the near future [1]. When discarded improperly, spent batteries represent 12% (%w/w) of the household waste, resulting an important pollution source in terms of heavy metal content [2].

Our interest is to find an advantageous technology for manganese recovery from spent Zn - Mn batteries trough sustainable process intensification and environmentally friendly process development. The conversion of the reacted manganese from spent household batteries to manganese dioxide through an electrochemical route represents an attractive opportunity both environmentally and economically.

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In recent years main interest has been focused on the development of new processes for recycling discarded materials; particularly on the possibility of high value metal recovery from spent batteries [3]. Numerous studies have been published regarding pyrometallurgical and hydrometallurgical routes for heavy metal recovery from low-grade ores and may be feasible for their recovery from spent batteries as well [4,5].

As earlier reported by different authors, the production of electrosynthetic MnO_2 (EMD) is carried out through the electrolysis of hot $MnSO_4$ and sulphuric acid solutions. Prior to the synthesis process, metals are leached away from their oxides with acid or alkali solutions or reacted in presence of an oxidizing or reducing agent [6,7] in order to completely or partially extract them from the solid to the liquid phase. Resulted liquors can be subjected to purification or can be processed as they are for MnO_2 electrowinning through anodic oxidation of Mn^{2+} ions present in the solution.

Choosing the adequate anodic material for the MnO_2 electrowinning process is essential. Large overpotential for the oxygen evolution reaction (OER), structural compatibility with the electrocrystallized material, chemical and electrochemical stability, ease of maintenance and cost-effectiveness are attributes of the appropriate substrate.

Literature reports a series of tested materials such as graphite [8], carbon nanotubes [9], lead and it's alloys with Sn, Sb, Ag [10] and lately titanium as anodic substrate because electrocrystallized EMD is of higher purity than one obtained on other substrates [11].

In the galvanic series of metals, titanium has a standard potential of −1.63 V which is close to aluminium. Therefore, titanium cannot be considered as being intrinsically noble. Yet, the excellent resistance of titanium to general corrosion in most environments is well known. This is the result of a stable protective surface film, which consists basically of TiO_2. This thin oxide film passivates titanium as long as the integrity of the film is maintained.

In electrochemical processes, when used as anodic material, the titanium's passivation is unwanted because of the low electric conductivity resulting in high-energy consumption. Nevertheless, in order to control this phenomenon several surface modification and passivation control techniques have been reported; literature lists as follows: surface coating with (3–5 *µm*) platinum film [12], heated platinum plated Ti anode [13], RuO_2 and IrO_2 coatings [14], anodic substrate activation through thermal-diffusion coating [15] β-PbO_2 coating and mixture of melted metallic titanium with graphite [11]. By surface modification with the previously listed techniques, a film can be developed which improves MnO_2 electrosynthesis on titanium.

When immersed in H_2SO_4, the dissolution of metallic titanium in the active state can be described by the presence of the following reactions [16]:

$$Ti \rightarrow Ti^{2+} + 2e^- \qquad \varepsilon^0 = -1.63 \text{ V/NHE} \qquad (1)$$

$$Ti \rightarrow Ti^{3+} + 3e^- \qquad \varepsilon^0 = -1.37\ V/NHE \qquad (2)$$

$$Ti \rightarrow Ti^{4+} + 4e^- \qquad \varepsilon^0 = -0.91\ V/NHE \qquad (3)$$

Since the lower valence titanium oxides are not stable in H_2SO_4 media [17], and no direct passivation can take place, reactions 1 and 2 have the highest probability to occur. Ma and Perré [18] suggest that metallic titanium corrosion in sulphuric acid (concentration range 0.1M – 1M) is due to the formation of the anion $[Ti(SO_4)_{2x}]^{-2x}$. With increasing acid concentration the formation of $[TiO_2(SO_4)_x]^{-2x}$ mainly occurs. These anions supposed to break down resulting in TiO_2.

According to M. Metikos et al. [19] the composition of the anodic film on titanium changes with increasing polarization resulting the following types of oxides:

$$TiH_x \rightarrow TiO \rightarrow Ti_2O_3 \cdot TiO_2 \rightarrow Ti_5O_9 \rightarrow Ti_6O_{11} \rightarrow Ti_3O_5 \rightarrow TiO_2 \quad (4)$$

Information about the manufacturing parameters of the titanium substrate becomes of interest because the substrate's crystal orientation highly promotes or retards the targeted oxide crystal formation [20] during MnO_2 electrosynthesis on Ti substrate with the following possible reactions [14]:

$$Mn^{2+} + 4H_2O \rightarrow MnO_4^- + 4H^+ + 2e^- \qquad \varepsilon^0 = 1.123\ V/\ NHE \qquad (5)$$

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \qquad \varepsilon^0 = 1.229\ V/\ NHE \qquad (6)$$

$$Mn^{2+} + 4H_2O \rightarrow MnO^-_4 + 8H^+ + 5e^- \qquad \varepsilon^0 = 1.51\ V/\ NHE \qquad (7)$$

$$MnO_2 + 2H_2O \rightarrow MnO^-_4 + 4H^+ + 3e^- \qquad \varepsilon^0 = 1.625\ V/\ NHE \qquad (8)$$

Titanium represents an efficient substrate for MnO_2 electrosynthesis from spent battery leach liquors, resulting in higher purity deposits and maintenance benefits by chemical and mechanical stability.

The aim of this study was to investigate the electrochemical behaviour of polarized metallic titanium in solutions similar in composition with one resulted from spent battery lixiviation, with application in MnO_2 electrosynthesis from the above solutions.

RESULTS AND DISSCUSIONS

Electrochemical corrosion measurements

Metallic titanium open circuit potential's (OCP) evolution was observed and registered, after immersion in 1M H_2SO_4 solutions in absence and presence of several Mn^{2+} concentrations (Figure 1).

A shift of the OCP values towards more positive potentials is observed in cases when different concentration of Mn^{2+} are present in the solution, as compared to metallic titanium in sulphuric acid solutions without additives, suggesting an interaction of Mn^{2+} with the anodic reaction of the corrosion process.

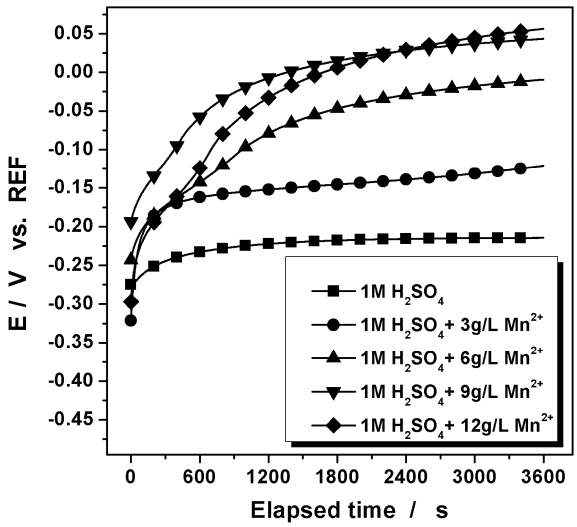

Figure 1. Titanium OCP evolution; Electrolyte: 1M H_2SO_4 in presence of several Mn^{2+} ion concentration [3 - 12g/L] Measurement duration: 1 h

The observed positivation of titanium OCP values with increasing Mn^{2+} concentration expresses an important decrease of the solutions corrosive effect on the titanium surface.

Polarization curves

Polarization measurements (Figure 2) were carried out in order to characterize the corrosion behaviour of the metallic titanium surface by applying the Stern - Geary theory [21], and by using Tafel interpretation.

According to the Stern-Geary theory, in the close vicinity of the open-circuit corrosion potential, the current density *i* is expressed by the following equation:

$$i = i_{corr}\ e^{[b_a(E-E_{corr})]} - e^{[b_c(E-E_{corr})]} \tag{9}$$

where b_a and b_c are the anodic and catodic activation coefficients.

Following the intricate active – passive behaviour of pure titanium in highly acidic sulphate solutions, the obtained polarization curves do not exhibit typical Tafel behaviour, and consequently an accurate evaluation of the corrosion parameters is not possible. However, the values of ε_{corr} and the corrosion current density, i_{corr}, were estimated near zero-overall current on the potential range of

±250 mV vs. OCP with a sweeping rate of 0.166 mVs^{-1}. Graphical representation of the polarisation curves is not shown. Evaluated parameters for the corrosion process are presented in Table 1.

Table 1. Parameters of the metallic titanium corrosion process

Solution	**ε_{corr} (mV vs. REF)**	**i_{corr} ($\mu A/cm^2$)**	**$-b_c^*$ (mV^{-1})**	**b_a^* (mV^{-1})**
1M H_2SO_4	-0.2	19	89	218
1M H_2SO_4+ 3g/L Mn^{2+}	-0.1	17	155	161
1M H_2SO_4+ 6g/L Mn^{2+}	0	15	98	139
1M H_2SO_4+ 9g/L Mn^{2+}	0.05	12	103	110
1M H_2SO_4+ 12g/L Mn^{2+}	0.04	10	86	118

*b_a and b_c are the Tafel anodic and cathodic activation coefficients

From the data presented in Table 1, positivation of the titanium's corrosion potential (ε_{corr}) and a slight diminishing of the corrosion current density can be noted, which corresponds to active corrosion inhibition of the metallic surface.

Voltammetry measurements

Linear voltammetry curves (LVC), presented in Figure 3, reveal four voltage regions: (i) active corrosion, (ii) active-passive transition, (iii) passivity and (iv) the voltage beyond which the dielectric breakdown of the passive film occurs. These observations are in good agreement with the cited literature [16, 22]. Each region from the polarization curve corresponds to different reactions, which occur with potential positivation.

Concurrent reactions [16] increase the number of geometrical faults in the formed TiO_2 layer and help the current passage.

The recorded polarization curves, with the addition of Mn^{2+} are presented in the inset of Figure 3, showing a clear dependence of the peak current with increasing Mn^{2+} concentration.

It is also notable that the presence of Mn^{2+} ions modifies the polarization curve's profile in region (iv), resulting in the breakdown of the insulating layer by the oxidation of manganese ions at ε_{ox}=~ 1.4 V/REF

MnO_2 electrocrystalization on metallic titanium in H_2SO_4 media occurs by the following global reaction:

$$Mn^{2+} + 2H_2O \rightarrow MnO_2 + 2e^- + 4H^+ \qquad \varepsilon^0 = 1.4 \text{ V/ NHE} \qquad (10)$$

EMD crystal structures have been observed on the titanium surface by scanning electron microscope (see section 4).

Occurrence of these manganese oxides on the anodic surface leads to structural faults in the TiO_2 film, which leads to the breakdown of the so formed titanium oxide thin film and allows the oxidative electrosynthesis to occur [17].

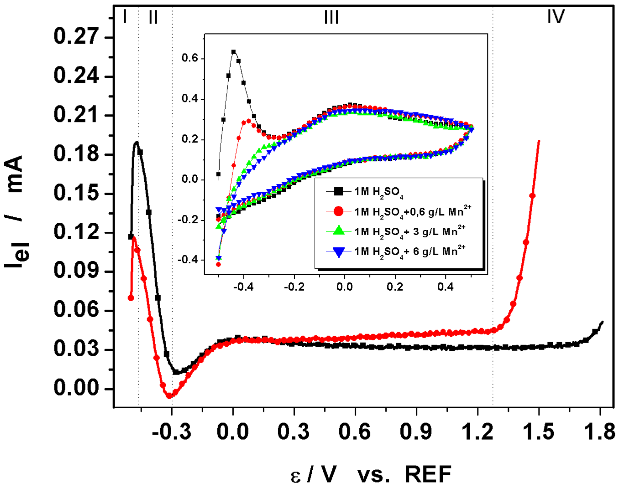

Figure 3. Metallic titanium polarization curves in the absence (■) and presence of Mn^{2+} ions (•). Inset: Titanium oxidation peak current evolution with the addition of different Mn^{2+} concentration

Activation of Ti electrode

Surface modification was required in order to use metallic titanium as a substrate for MnO_2 electrosynthesis. Several activation measurements have been performed in 1M H_2SO_4 and different concentrations of Mn^{2+}. By visual examination, an increasing number of MnO_2 germination centres on titanium have been noted with increasing manganese(II) ion concentration and have been considered for the further applied surface activation protocol.

Under potentiostatic control the previously cleaned (as described in the experimental section), metallic titanium (Figure 5a) was subjected to polarization in a solution with Mn^{2+} concentration similar with one resulted from spent battery lixiviation. During this process electrolytic manganese dioxide crystals developed as shown in Figure 5b.

The electrode surface modification was achieved in two steps and represents the surface activation protocol.

Metallic titanium has been immersed in a solution containing 6g/L Mn^{2+}. In the first step (S1) the potential was modified with 2 mVs^{-1} in the range from 0 to 1.5V/ REF. During the second step (S2) the potential was modified in the range from 1.5 to 1.7V/ REF with $2mVs^{-1}$.

Preparation of the electrode by polarization technique in the first (S1) potential domain leads to the formation of a mixed TiO_x and MnO_X oxide film which protects the surface from passivation. During the second step (S2), by visual examination, the number of germination centres formed during S1 did not increase; growth of the existing crystalline formations has been noted. The switch from S1 to S2 was made by current interruption for 1 second and was considered responsible for the crystal growth instead of germination centre multiplication.

The potential value was varied below MnO_4^- formation and oxygen evolution reaction at the electrochemical conditions.

Manganese dioxide electrosynthesis tests

The activated titanium electrode was inserted in a divided cell setup, composed by a modified titanium electrode (MTE), platinum counter electrode (PCE), Ag||AgCl/KCl_{sat} reference electrode and a porous ceramic material for MTE separation from PCE.

During 4 hours of continuous electrolysis the MTE did not exhibit passivation or critical behaviour (Figure 4).

Under continuous stirring and constant temperature (22°C) a film of MnO_2 was deposited (Figure 5c) on the modified titanium surface from acidic spent battery leach liquor with an average concentration of 6 g/L Mn^{2+}.

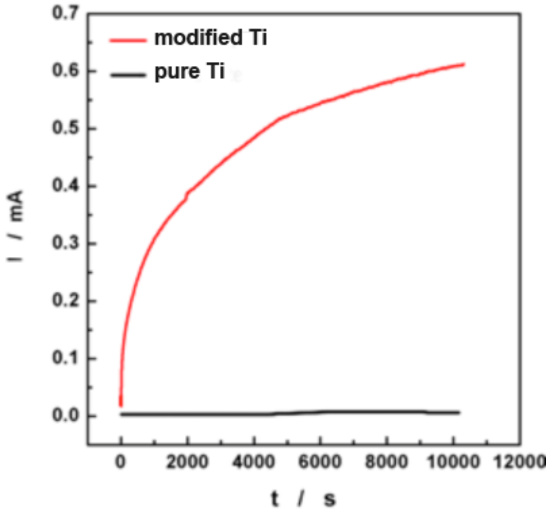

Figure 4. Current evolution on the pure and modified titanium electrode during potentiostatic electrolysis; working anodic potential ε = +1.7V/REF; Electrolyte: 1M H_2SO_4 (pH=0.5); Mn^{2+} 6g/L; w = 500 rpm

Surface and composition characterization of MTE

The electrode surface has been characterized by imaging techniques. After chemical treatment the titanium shows pitting corrosion morphologies (Figure. 5a), which underlines the treatment's efficiency regarding existing oxide removal as shown in Table 2. After electrolysis the manganese dioxide was observed as a compact crystalline formation localized on the metallic surface.

The deposit morphology has been determined by scanning electron microscopy (SEM) (Quanta 3D FEG). EDAX X-ray dispersive energy analyser attached to the SEM has been used to determine the chemical composition of the electrodeposited MnO_2. Results are shown in Table 3.

Table 2. EDAX analysis for metallic titanium surface

Element	Wt %	At %
N/A	1.72	0.37
Ti	98.28	99.63

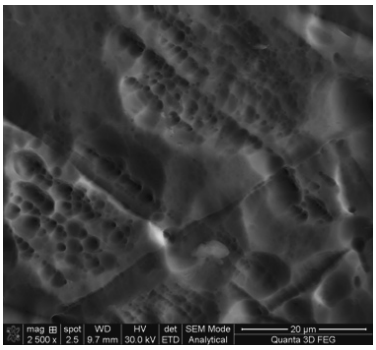

Figure 5a. Pure metallic titanium surface before activation protocol;

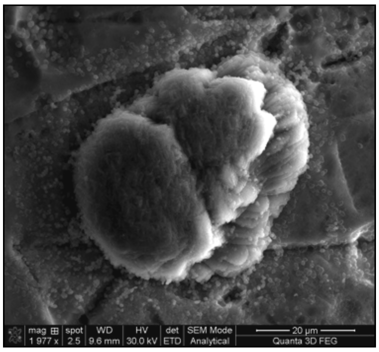

Figure 5b. Manganese dioxide germination on Ti–after S2 step; Electrolyte: 1M H_2SO_4 + 6g/L Mn^{2+}, pH=~0.5, sweep rate $2mVs^{-1}$

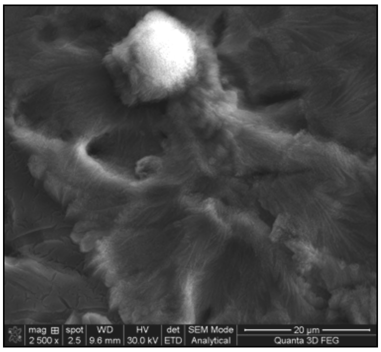

Figure 5c. Electrolytic manganese dioxide deposit after 3 hours electrosynthesis; Electrolyte: spent battery leach liquors, pH=~0.5, 6g/L Mn^{2+}, 1M H_2SO_4

In Figure 5b, electrolytic germination of manganese dioxide obtained after activation procedure S2 can be observed. Figure 5c. represents SEM imaging of the obtained MnO_2 deposit by potentiostatic electrolysis. The resulted crystal structure does not resemble specific manganese crystallization morphology but similar features with the electroactive γ - MnO_2 form can be observed.

Table 3. EDAX analysis for deposited MnO_2 (EMD)
on the modified titanium surface

Element	Wt %	At %
Mn	21.71	10.47
S	25.68	21.23
O	37.32	61.83
Ti	1.84	1.02
N/A	13.45	5.45

CONCLUSIONS

The influence of manganese (II) inclusion was studied on the electrochemical behaviour of commercially pure titanium in acidic electrolytes through open circuit potential measurements.

The presence of Mn^{2+} ions in the acidic electrolyte maintains good electric conductivity caused by formation of a mixed oxide film on the electrode surface. Based on these assumptions, a titanium surface activation technique was developed which allows MnO_2 electrosynthesis.

MnO_2 deposited during anodic polarization on the titanium surface, act as nucleation centre for the latter developing EMD film.

Commercially pure titanium anode surface modification prior to MnO_2 electrodeposition from spent battery leach liquors is essential.

By surface modification, titanium passivation has been delayed during anodic polarisation, from several tents of minutes as described in the literature, to several hundred minutes in our experimental conditions.

EXPERIMENTAL PART

Electrode preparation

The working electrode used in our experiments consisted of a 1 cm^2 titanium cylinder (ϕ = 2 mm). Before each measurement, in order to remove any pre-existing oxide film, the titanium surface was immersed for 33 seconds in a mixture composed of 25% HF and 75% HNO_3, washed with double distilled water, patted dry with a lint-free cloth then immersed in the electrolyte within the electrochemical cell.

Electrochemical cell and electrolytes

The cell used in this study consisted of a graded glass flask, in which the titanium working electrode and platinum counter electrode was immersed. In all measurements $Ag||AgCl/KCl_{sat}$ reference electrode (REF) was used. Before every experiment a magnetic stirrer was used for oxygen and hydrogen bubbles removal.

Solutions were prepared from *Merck* 98% H_2SO_4, *J.T. Baker* $MnSO_4$ (mono-hydrate) and double distilled water, without further purification.

Spent Zn-Mn batteries have been manually dismantled by removing external casing followed by the removal of the metal caps and plastic grommets. Remaining Zn anode and MnO_2 cathode were carefully separated and weighted. The resulted black powder was leached with 1M H_2SO_4 for 1 hour at room temperature.

Used equipment and software

For solid and liquid analysis Avanta PM GBC atomic absorption spectrophotometer was used. For surface characterization a scanning electron microscope (SEM) (Quanta 3D FEG) was used. For surface chemical analysis EDAX X-ray dispersive energy analyser attached to the SEM was applied.

Liquid and solid phases obtained during this study have been analysed by atomic absorption (AAS) technique for composition determination.

Electrochemical measurements have been done with PC controlled PARSTAT 2273 and Daltronix Electrochemical System, composed by DXC 238 potentiostat connected to a PC trough National Instruments (NI) DAQ hardware. Software packages used have been developed in our laboratory in NI Labview environment.

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REFERENCES

1. European Commission, Eurostat, Publications Office of the European Union, **2010**, 148-149.
2. I. De Michelis, F. Ferella, E. Karakaya, F. Beolchini, F. Veglio, *Journal of Power Sources*, **2007**, *172*, 975.
3. E. Sayilgan, T. Kukrer, G. Civelekoglu, F. Ferella, A. Akcil, F. Veglio, M. Kitis, *Hydrometallurgy*, **2009**, *97*, 158.
4. Wensheng Zhang, Chu Yong Cheng, *Hydrometallurgy*, **2007**, *89*, 137.
5. A.A. Baba, A.F. Adekola, R.B. Bale, *Journal of Hazardous Materials*, **2009**, *171*, 838.
6. E. Sayilgan, T. Kukrer, F. Ferella, A. Akcil, F. Veglio, M. Kitis, *Hydrometallurgy*, **2009**, *97*, 73.
7. Shun Myung Shin, Gamini Senanayake, Jeong-sooSohn, Jin-gu Kang, Dong-hyo Yang, Tae-hyun Kim, *Hydrometallurgy*, **2009**, *96*, 349.
8. Keqiang Ding, *International Journal of Electrochemical Science,* **2010**, *5*, 668 .
9. Yaohui Wang, Hao Liu, Xueliang Sun, Igor Zhitomirsky, *Scripta Materialia*, **2009**, *61*, 1079.
10. P. Ilea, I.-C. Popescu, M. Urda, L. Oniciu, *Hydrometallurgy*, **1997**, *46*, 149.
11. P. Ilea, “Electrosinteze anorganice”, Casa Cărții de Știință, **2005**, 167.
12. A.G. Kholmogorov, A.M. Zyzhaev, U.S. Kononov, G.A. Moiseeva, G.L. Pashkov, *Hydrometallurgy*, **2001**, *56*, 1.

13. Yu. S. Kononov, G.L. Pashkov, V.V. Patrushev, A.G. Kholmogorov, V.P. Plekhanov, *Zhurnal Prikladnoi Khimii*, **2007**, *80*, 339.
14. Qifeng Wei, Xiulian Ren, Jie Du, Sijie Wei, SuRong Hu, *Minerals Engineering*, **2010**, *23*, 578.
15. S.V. Skopov, S.S. Naboichenko, L.I. Galkova, *Tsvetnaya Metallurgiya*, **2009**, *1*, 25.
16. W.B. Utomo, S.W. Donne, *Electrochimica Acta*, **2006**, *51*, 3338.
17. Z. Abdel Hady, J. Pagetti, *Journal of Applied Electrochemistry*, **1976**, *6*, 333.
18. Chuk-Ching Ma, Ernest M. Peres, *Industrial and Engineering Chemistry*, **1951**, *43*, 675.
19. M. Metikos-Hukovic, *Surface Technology*, **1985**, *24*, 273.
20. Gerd Lütjering, James C. Williams, *Engineering Materials and processes - Titanium – 2nd edition*, Springer, **2007**.
21. M. Stern, A.L. Geary, *Journal of Electrochemical Society*, **1957**, *104*, 56.
22. S.M.A. Hosseini, V.B. Sigh, *Materials Chemistry and Physics,* **1993**, *33*, 63.