

Anodic Oxidation of Sulphite in Alkaline Solutions on Skeletal Nickel Electrode. I. Voltammetric Studies

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Abstract: In this paper, anodic oxidation of sulphite ions on skeletal nickel electrode in aqueous alkaline solution was investigated in order to find the relationship between the concentration of sulphite in a solution and kinetic parameters. The research is necessary to understand the oxidation mechanism on the surface of this type of electrodes, taking into account that skeletal nickel electrode is a very interesting material for the catalysis of both chemical and electrochemical sulphite oxidation reactions. Electrochemical behavior of sulphite ions has been studied by cyclic voltammetry and linear polarization.

Keywords: skeletal nickel, sulphite anodic oxidation, cyclic voltammetry, linear polarization, electrochemical kinetic parameters.

1. Introduction

During the last century, the development of our society has been intimately connected to an abundant supply of cheap carbon to fuel our ever-growing economy. In 2010 from the world's total energy demand, fossil fuels represented just over 80% [1].

Electrochemical energy devices, which store and transform energy, are a key technology for industries. A large number of electrochemical energy technologies have been developed in the past. These systems continue to be optimized in terms of cost, life time, and performance, leading to their constant expansion in existing and emerging market sectors [1].

Fuel cells are considered to be the green power sources. All fuel cells consist of two electrodes in which electrochemical reactions occur, separated by an electrolyte made of an electrically ionic conducting media. This separates the reactants and forces the electrons to travel in an external circuit to induce a current while the ionic charge carriers migrate through the electrolyte to complete the cell reactions [2].

A wide variety of fuel cell systems of different scales (few W to MW range) are now commercially available and their operating regimes and widely varying performance characteristics have been discussed in the literature. These devices have traditionally been categorized firstly by the type of electrolyte and then by the type of fuel used [1-4].

Initially, sulphur compounds were classified as contaminants in fuel gas, especially H₂S, and they are known as poisoning agents which cause premature degradation of the Molten Carbonate Fuel Cells (MCFC). Furthermore, fuel gas often contains sulphur dioxide which in contact with the cathode causes a degradation of the fuel cell performance by corrosion and poisoning the electrodes.

A number of new fuel cells, which will have positive effect on the environment, and the way we produce and utilize energy, will be developed in the

future. Subsequently, the sulphur dioxide-oxygen fuel cell would play an important role due to the possibility to obtain simultaneously both electric energy and sulphuric acid.

Platinum electrodes equipped cells to obtain a 90% conversion of SO₂, even in case when the gas concentration in anodic area was low. Due to the platinum high price has been followed the preparation cheaper electrodes with similar catalytic activities [5].

The sulphur compounds are very reactive and may exist in many oxidation states. Nevertheless, sulphite ions are stable in alkaline media. The oxidation of sulphite under alkaline conditions has been studied in order to find new electrode materials with high catalytic activity. The researches started from the premise that used electrodes must have as well catalytic properties for oxygen evolution reaction (OER). In this case nickel is frequently used to obtain anodes for OER. The problem associated with long-term electrochemical application is that the anode potential is not stable in time, which causes an increase in energy consumption [6]. Improvement was made by alloying nickel with different elements. A significant amount of research dedicated to improve the efficiency of OER in alkaline media with more durable electrode materials such as skeletal nickel [7].

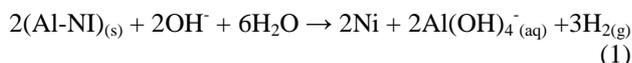
In this paper, cyclic voltammetry and linear polarization techniques were used in order to characterize the anodic sulphite oxidation in alkaline solutions on skeletal nickel electrode.

2. Experimental

2.1. Electrode preparation

Skeletal nickel electrode was prepared using thermal arc spraying technique. For skeletal Ni electrodes preparation Ni (Fluka, 99.2%) and Al (Fluka, 99.5%) have

been used as anode, respectively as cathode. During the thermal spray the arc current and voltage were set to 200 A and 30 V. In order to remove Al from the coating, the samples were submitted to alkaline leaching in 1 mol L⁻¹ NaOH solution at about 80°C, for 2 h [8]. Finally, the electrodes were cleaned for 15 minutes in an ultrasonic bath using distilled water. The chemical reaction of Al dissolution is [9]:



Skeletal nickel electrode prepared using this method has a high surface area and increased activity for followed anodic processes in alkaline media e.g. sulphite oxidation and OER [10].

2.2. Electrochemical measurements

Cyclic and linear voltammetric measurements were performed using a SP 150 Bio-Logic potentiostat/galvanostat. A three-electrode cell configuration was used consisting of two graphite counter electrodes placed symmetrically to the working electrode - Ni skeletal and Ag/AgCl as reference electrode. All potentials are given versus the reference electrode.

Cyclic voltammograms were recorded at different scan rate between 5 and 500 mV s⁻¹. Linear polarization curves were registered potentiostatically in 1 mol L⁻¹ NaOH (prepared using Merck NaOH, p.a.) solution in the absence and presence of Na₂SO₃ (Merk, p.a. min. 98%) with 1 mV s⁻¹ scan rate. Different concentrations of Na₂SO₃ added were: 10⁻³, 10⁻² and 10⁻¹ mol L⁻¹.

2.3. Surface analysis

Surface morphology of the electroactive skeletal nickel electrode after dissolution of Al was evaluated by scanning electron microscopy (SEM) using a Quanta FEG 250 (FEI, The Netherlands) scanning electron microscope (SEM) equipped with EDX analyzer.

3. Results and Discussion

3.1. SEM and EDX analyses

EDX spectrum for nickel skeletal electrode used in voltammetric studies is presented in figure 1.

EDX analysis revealed that the working electrode contain only nickel (92.1%) and aluminum (5.2%). The presence of sodium (0.6%) and oxygen (2.1%) is attributed to the residual NaOH solution. Composition is given in weight percents.

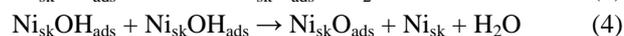
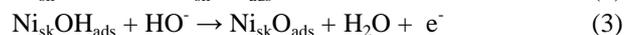
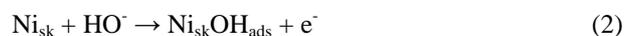
Scanning electron micrographs of the skeleton Ni electrode after electrochemical studies are presented in figure 2 a-c at different magnification.

These figures shown relevant images for typical structure of skeletal nickel electrode used in the present study. The surface resembling a complex, three-dimensional nickel matrix with high roughness.

3.2. Cyclic voltammetry studies

A typical cyclic voltammograms recorded on skeletal nickel electrode in alkaline solution are depicted in figure 3.

On the anodic plateau only OER is visible. The OER mechanism on skeletal nickel electrode is similar with the same process on Ni-Sn [11] or Ni-Co [12] electrodes. This mechanism adopted for alkaline media was proposed first time by Iwakura [13] and was proved by Trasatti [14] and can be described by following reactions [11-13]:



The process is controlled by charge-transfer step of the adsorbed hydroxyl species formation on skeletal nickel surface active site (Ni_{sk}). The formation of oxygen molecules occurs by recombination of two adjacent adsorption site obtained in reaction (3) and (4).

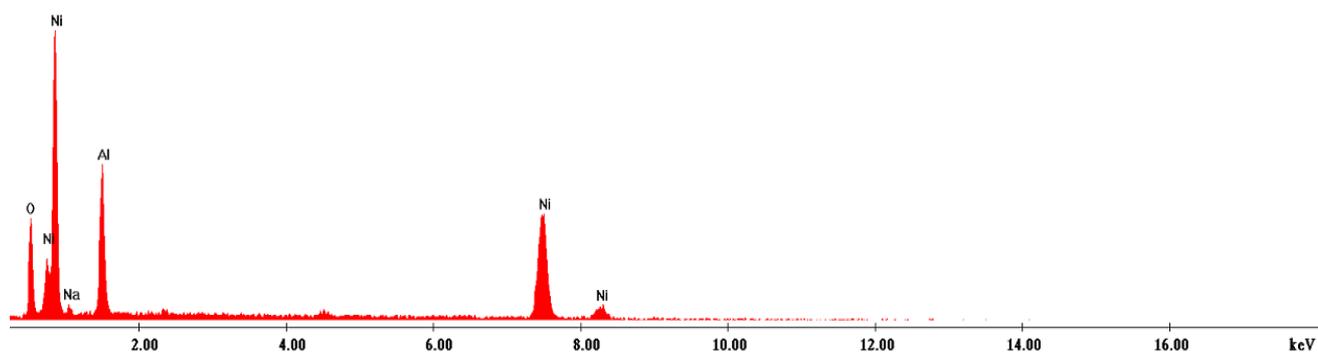


Figure 1. EDX spectrum for nickel skeletal electrode after electrochemical studies

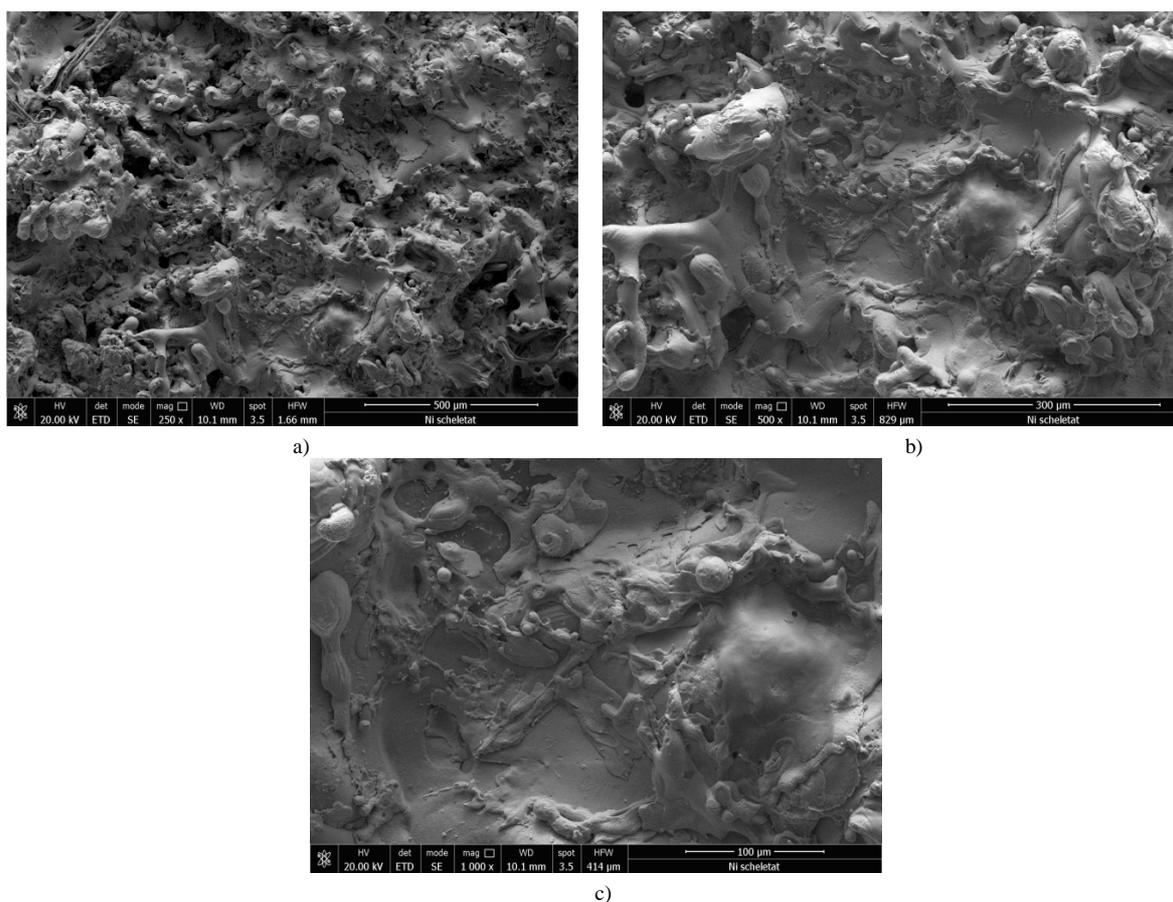
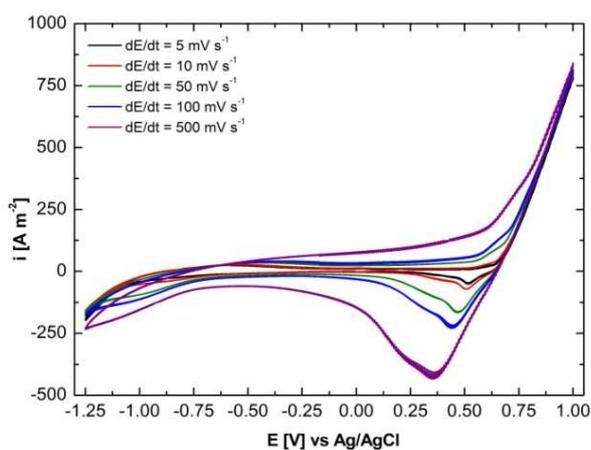
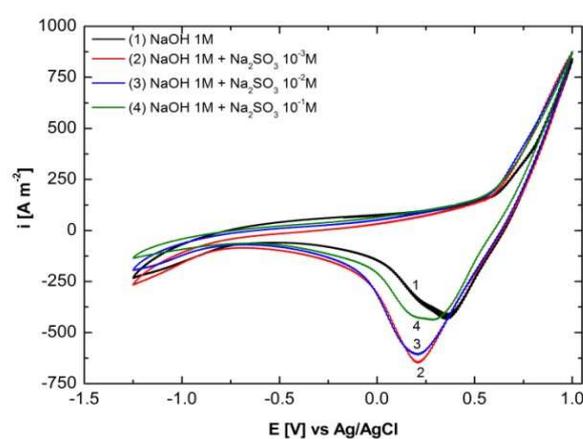


Figure 2. SEM micrographs of the skeletal nickel electrode surface after voltammetric studies in alkaline media

Figure 3. Cyclic voltammograms recorded on skeletal nickel electrode in 1 mol L^{-1} NaOH at different polarization rate

Cyclic voltammograms plotted with high scan rate (500 mV s^{-1}) on skeletal nickel electrode in alkaline electrolyte in which were added different amounts of sodium sulphite are shown in figure 4.

Figure 4. Cyclic voltammograms recorded on skeletal nickel electrode in 1 mol L^{-1} NaOH without/with different concentration of Na_2SO_3 at 500 mV s^{-1}

From the analysis of cyclic curves a separation of characteristic peaks for SO_3^{2-} ions oxidation to SO_4^{2-} does not observed.

In electrolyte solutions containing sodium sulphite, the potential of anodic oxygen evolution, respectively the potential of cathodic hydrogen evolution, on the surface of the working electrode are shifted to more negative values.

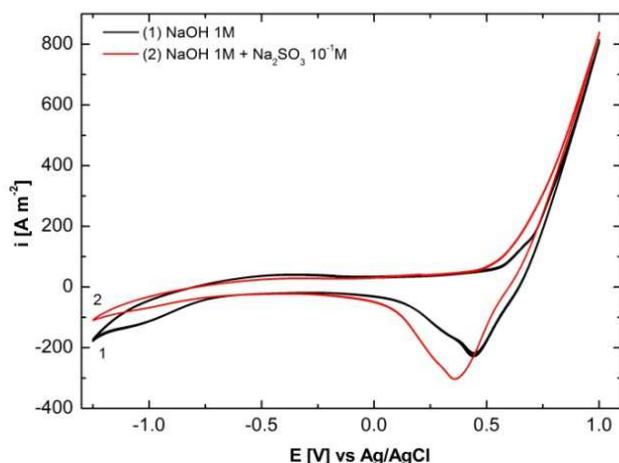


Figure 5. Cyclic voltammograms recorded on skeletal nickel electrode in 1 mol L⁻¹ NaOH without/with 10⁻¹ mol L⁻¹ Na₂SO₃ at 100 mV s⁻¹

On cyclic curves plotted at 100 mV s⁻¹ shown in figure 5 for 1 mol L⁻¹ NaOH solutions in absence and presence of 10⁻¹ mol L⁻¹ Na₂SO₃ major changes are not observed on anodic plateau.

Decreasing the scan rate at 10 mV s⁻¹ (figure 6) provides the opportunity to make a first identification of the SO₃²⁻ ions oxidation processes occurring at the interface skeletal nickel electrode / electrolyte in potential range between +0.4 and +0.5 V/Ag/AgCl.

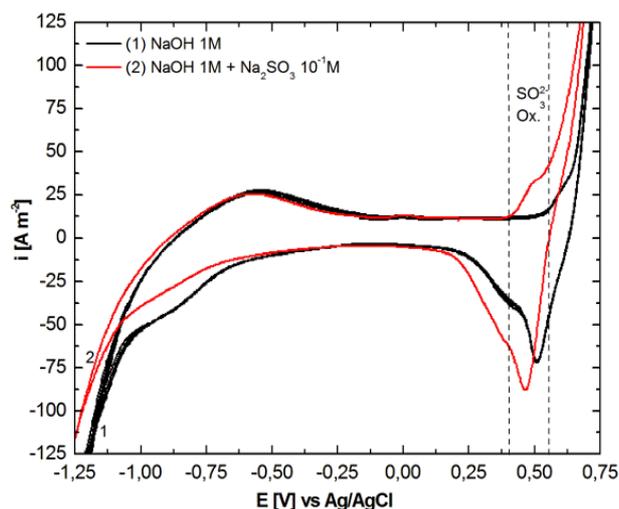


Figure 6. Cyclic voltammograms recorded on skeletal nickel electrode in 1 mol L⁻¹ NaOH without/with 10⁻¹ mol L⁻¹ Na₂SO₃ at 10 mV s⁻¹

3.3. Linear voltammetry studies

Experimental technique by which have been confirmed the results presented above was linear voltammetry at low scan rate (5 mV s⁻¹), the curves obtained in alkaline media with SO₃²⁻ ions are shown in figure 7.

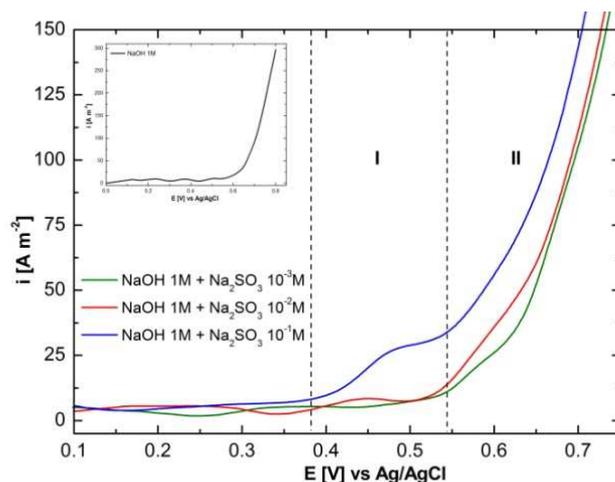
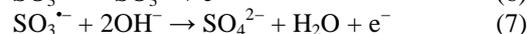


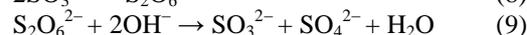
Figure 7. Linear voltammograms recorded on skeletal nickel electrode in 1 mol L⁻¹ NaOH with 10⁻¹ mol L⁻¹ Na₂SO₃ at 5 mV s⁻¹; linear voltammograms in 1 mol L⁻¹ NaOH inserted

From the analysis of linear voltammograms, specific potential ranges of both oxidation processes that occur at the interface electrode/electrolyte (SO₃²⁻ ions oxidation (I) and OER (II)) has been emphasized.

The electrochemical oxidation of sulphite to sulphate ions in alkaline media, corresponding to plateau I, can be described using two possible mechanisms, presented by Skavas [15]. According to the first one, sulphite anion is oxidized to sulphate in two successive steps, each implying one electron transfer:



In the second mechanism, sulphite anion is oxidized to sulphite radical (reaction 6). In next step two sulphite radicals can interact forming dithionate ions S₂O₆²⁻. Finally, these ions consecutively disproportionate in sulphate and sulphite ions:



In the second potential ranges from figure 7 the OER mechanism on skeletal nickel electrode takes place following reactions 2 - 5 and SO₃²⁻ ions oxidation is conducted directly in alkaline electrolyte by a chemical irreversible process:



in which the molecular oxygen was produced on electrode surface in oxygen evolution anodic reaction. As presented above, we can affirm that the plateau I corresponds to electrochemical oxidation of sulphite and the second one to the chemical oxidation.

Based on linear voltammograms, kinetic parameters (transfer coefficient - α and exchange current density- i_0) for electrochemical oxidation of sulphite to sulphate in alkaline solution on skeletal nickel electrode have been

calculated for each electrolyte solution, using Tafel method, shown in figure 8. The calculated kinetic parameters are presented in table 1.

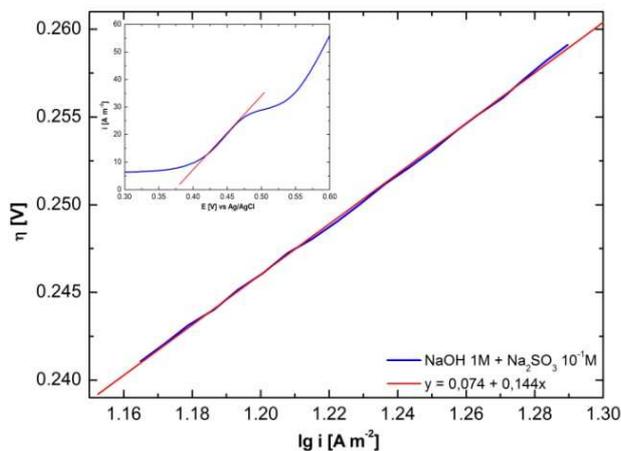


Figure 8. Tafel slope for electrochemical oxidation of SO_3^{2-} oxidation in alkaline media

TABLE 1. The kinetic parameters for sulphite oxidation in alkaline solutions

Na_2SO_3 concentration [mol L ⁻¹]	b [mV dec ⁻¹]	α	i_o [A m ⁻²]
10 ⁻¹	144	0.40	16.10
10 ⁻²	176	0.33	15.63
10 ⁻³	201	0.29	15.33

Inspection of obtained data emphasises an increase of exchange current density and anodic transfer coefficient with SO_3^{2-} ions concentration added in alkaline media.

4. Conclusions

Skeletal nickel electrode has proved to be a very interesting material for the catalysis of both chemical and electrochemical reactions.

Voltammetric studies presented have confirmed the possibility to oxidize electrochemically SO_3^{2-} to SO_4^{2-} on skeletal nickel electrode.

From the perspective of using skeletal nickel as potential electrode materials in fuel cells, the possibility to

oxidize sulphite ions directly on their surface, provides a good reason for continue studies presented in this paper by chronoamperometric experiments in order to determine the oxidation process efficiency. Further, electrochemical impedance spectroscopy studies are necessary for a complete characterization of sulphite anodic oxidation in alkaline solutions.

ACKNOWLEDGEMENT

This work was partially supported by University Politehnica Timisoara in the frame of PhD studies.

REFERENCES

1. Badwal S.P.S., Giddey S., Kulkarni A. and Munnings C., *Journal of the Australian Ceramic Society*, 50, **2014**, 23–37.
2. Rexed I., Applications for Molten Carbonate Fuel Cells, Doctoral Thesis, **2014**, KTH Royal Institute of Technology, School of Chemical Science and Engineering, Department of Chemical Engineering and Technology Applied Electrochemistry, Stockholm, Sweden.
3. Devanathan R., *Energy & Environmental Science*, 1, **2008**, 101–119.
4. Badwal S.P.S., Giddey S.S., Munnings C., Bhatt A.I. and Hollenkamp A.F., *Frontiers in Chemistry*, 2(79), **2014**, 1–28.
5. Bagotsky V.S., *Fuel cells: problems and solution*, 2nd Edition, Ed. John Wiley & Sons, **2012**.
6. Miao H.J. and Piron D.L., *Journal of Applied Electrochemistry*, 21, **1991**, 55–59.
7. Martinez W.M., Fernandez A.M., Cano U. and Sandoval J.A., *International Journal of Hydrogen Energy*, 35, **2010**, 8457–8462.
8. Kellenberger A., Vaszilcsin N., Brandl W. and Duteanu N., *International Journal of Hydrogen Energy*, 32(15), **2007**, 3258–3265.
9. Trefilov M.I., Cucu A., Iordache S., Serban E.C., Banu N., Marinescu A., Andronie A., Ceaus C., Stamatina S., Ceaus M., Emandia A., Nan G. and Stamatina I., *Optoelectronics And Advanced Materials – Rapid Communications*, 4 (11), **2010**, 1733 - 1735.
10. Duteanu N., Vaszilcsin N., Kellenberger A., Dan M. and Barbatei M., *Chem. Bull. "POLITEHNICA" Univ. (Timisoara)*, 60(74), 1, **2015**, 1–4.
11. Jovic B.M., Lacnjevac U.C., Jovic V.D., Krstajic N.V., *Journal of Electroanalytical Chemistry*, 754, **2015**, 100–108.
12. Wu G, Li N, Zhou D.R., Mitsuo K., Xu B.Q., *Journal of Solid State Chemistry*, 177, **2004**, 3682–3692
13. Iwakura C., Fukuda K., Tamura H., *Electrochimica Acta*, 21, **1976**, 501–508.
14. Trasatti S., Electrode kinetics and electrocatalysis of hydrogen and oxygen electrode reaction, Ed. H.Wendt, *Electrochemical Hydrogen Technologies*, Elsevier, Amsterdam, **1990**.
15. Skavas E., Hemmingsen T., *Electrochimica Acta*, 52, **2007**, 3510–3517.

Received: 17 December 2015

Accepted: 27 January 2016