University of Belgrade, Technical Faculty in Bor

29th International Conference Ecological Truth & Environmental Research

EcoTER'22

Proceedings

Editor
Prof. Dr Snežana Šerbula

21-24 June 2022, Hotel Sunce, Sokobanja, Serbia

University of Belgrade, Technical Faculty in Bor

29th International Conference Ecological Truth & Environmental Research

EcoTER'22

Proceedings

Editor
Prof. Dr Snežana Šerbula

21-24 June 2022, Hotel Sunce, Sokobanja, Serbia

PROCEEDINGS

29th INTERNATIONAL CONFERENCE

ECOLOGICAL TRUTH AND ENVIRONMENTAL RESEARCH – EcoTER'22

Editor:

Prof. Dr Snežana Šerbula

University of Belgrade, Technical Faculty in Bor

Technical Editors:

Dr Jelena Milosavljević

University of Belgrade, Technical Faculty in Bor

Asst. Prof. Dr Ana Radojević

University of Belgrade, Technical Faculty in Bor

Dr Jelena Kalinović

University of Belgrade, Technical Faculty in Bor

Asst. Prof. Dr Tanja Kalinović

University of Belgrade, Technical Faculty in Bor

Asst. Prof. Dr Žaklina Tasić

University of Belgrade, Technical Faculty in Bor

Publisher: University of Belgrade, Technical Faculty in Bor

For the Publisher: Prof. Dr Nada Štrbac, Dean

Printed: GRAFIK CENTAR DOO Beograd, 120 copies

Year of publication: 2022

ISBN 978-86-6305-123-2

CIP - Каталогизација у публикацији
Народна библиотека Србије, Београд

502/504(082)(0.034.2)
574(082)(0.034.2)

INTERNATIONAL Conference Ecological Truth & Environmental Research (29 ; 2022 ; Sokobanja)

Proceedings [Elektronski izvor] / 29th International Conference Ecological Truth and Environmental Research - EcoTER'22, 21-24 June 2022, Sokobanja, Serbia ; [organized by University of Belgrade, Technical faculty in Bor (Serbia)] ; [co-organizers University of Banja Luka, Faculty of Technology – Banja Luka (B&H) ... [et al.]] ; editor Snežana Šerbula. - Bor : University of Belgrade, Technical faculty, 2022 (Beograd : Grafik centar). - 1 USB fleš memorija ; 5 x 5 x 1 cm

Sistemski zahtevi: Nisu navedeni. - Nasl. sa naslovne strane dokumenta. - Tiraž 120. - Bibliografija uz svaki rad. - Registar.

ISBN 978-86-6305-123-2

а) Животна средина -- Зборници б) Екологија -- Зборници

COBISS.SR-ID 69053705

29th International Conference
Ecological Truth and Environmental Research 2022

is organized by:

UNIVERSITY OF BELGRADE, TECHNICAL FACULTY IN BOR (SERBIA)

Co-organizers of the Conference:

University of Banja Luka, Faculty of Technology – Banja Luka (B&H)

University of Montenegro, Faculty of Metallurgy and Technology – Podgorica (Montenegro)

University of Zagreb, Faculty of Metallurgy – Sisak (Croatia)

University of Pristina, Faculty of Technical Sciences – Kosovska Mitrovica

Association of Young Researchers – Bor (Serbia)

The Conference is financially supported by

the Ministry of Education, Science and Technological

Development of the Republic of Serbia

Platinum Donor of the Conference

HONORARY COMMITTEE

Dr Petar Paunović, Zaječar (Serbia)

Prof. Dr Stevan Stanković, Bor (Serbia)

Prof. Dr Zvonimir Stanković, Bor (Serbia)

Prof. Dr Velizar Stanković, Bor (Serbia)

Dragan Ranđelović, Society of Young Researchers – Bor (Serbia)

Toplica Marjanović, Society of Young Researchers – Bor (Serbia)

Mihajlo Stanković, Special Nature Reservation of Zasavica, Sremska Mitrovica (Serbia)

SCIENTIFIC COMMITTEE

ORGANIZING COMMITTEE

Prof. Dr Snežana Šerbula, *President*

Prof. Dr Snežana Milić, *Vice President*

Prof. Dr Đorđe Nikolić, *Vice President*

Prof. Dr Milica Veličković (Serbia)

Prof. Dr Danijela Voza (Serbia)

Prof. Dr Maja Nujkić (Serbia)

Dr Ana Simonović (Serbia)

Dr Tanja Kalinović (Serbia)

Dr Ana Radojević (Serbia)

Dr Žaklina Tasić (Serbia)

Dr Jelena Kalinović (Serbia)

Dr Jelena Milosavljević (Serbia)

Dr Dragana Medić (Serbia)

Aleksandra Papludis, MSc (Serbia)

Sonja Stanković, MSc (Serbia)

Vladan Nedelkovski, MSc (Serbia)

Mara Manzalović, English language teacher (Serbia)

Enisa Nikolić, English language teacher (Serbia)

PREFACE

In today's world, the environment has been endangered by the use of outdated technology, fossil fuels and environmental law violations. Therefore, environmental and many other scientists all over the world have been concerned about finding sustainable technology in resolving these issues. That is why environmental research and ecological truth are at the focus of the 29th International Conference Ecological Truth & Environmental Research 2022 (EcoTER'22), which will be held in Sokobanja, Serbia, 21–24 June 2022. On behalf of the Organizing Committee, it is a great honor and pleasure to wish all the participants a warm welcome to the Conference.

We hope to convey the message of the conference, which is that a transformation of attitudes and behavior would bring the necessary changes. This is also an opportunity for the participants who are experts in this field to exchange their experiences, expertise and ideas, and also to consider the possibilities for their collaborative research.

The 29th International Conference Ecological Truth & Environmental Research 2022 is organized by the University of Belgrade, Technical Faculty in Bor, and co-organized by the University of Banja Luka, Faculty of Technology, the University of Montenegro, Faculty of Metallurgy and Technology – Podgorica, the University of Zagreb, Faculty of Metallurgy – Sisak, the University of Pristina, Faculty of Technical Sciences – Kosovska Mitrovica and the Association of Young Researchers, Bor.

These proceedings include 85 papers from the authors coming from the universities, research institutes and industries in 6 countries: Bulgaria, Italia, Albania, Bosnia and Herzegovina, Montenegro and Serbia.

As a part of this year's conference, the 4th Student section – EcoTERS'22 is being held. We appreciate the contribution of the students and their mentors who have also participated in the Conference.

Financial assistance provided by the Ministry of Education, Science and Technological Development of the Republic of Serbia is gratefully acknowledged by the Organizing Committee of the EcoTER'22 conference.

The support of the Platinum donor and their willingness and ability to cooperate have been of great importance for the success of EcoTER'22. The Organizing Committee would like to extend their appreciation and gratitude to the Platinum donor of the Conference for their donation and support.

We appreciate the effort of all the authors who have contributed to these Proceedings. We would also like to express our gratitude to the members of the scientific and organizing committees, reviewers, speakers, chairpersons and all the Conference participants for their support to EcoTER'22. Sincere thanks go to all the people who have contributed to the successful organization of EcoTER'22.

Prof. Snežana Šerbula,

President of the Organizing Committee

TABLE OF CONTENTS

Plenary Lectures

Conference Papers

29th International Conference Ecological Truth & Environmental Research
21 - 24 June 2022, Hotel Sunce, Sokobanja, Serbia
www.eco.tfbor.bg.ac.rs

SYNTHESIS AND CHARACTERISATION OF Ti/SnO_2-Sb-TYPE DSA ANODES FOR WASTEWATER TREATMENT

Vladan Nedelkovski[1*], Sonja Stanković[1], Milan Radovanović[1], Milan Antonijević[1]
[1]University of Belgrade, Technical faculty in Bor, V.J. 12, 19210 Bor, SERBIA
[*]*vnedelkovski@tfbor.bg.ac.rs*

Abstract

In this paper, two Ti/SnO_2-Sb-type anodes were syntesised via thermal decomposition method, one of which was doped with Mn and Cr in order to achieve increased number of active sites and prolonged service life of said anodes. Six layers of precursor solution were applied on the titanium substrate before the final step of calcination at 550 °C. The characterisation of synthesised anodes comprised of different electrochemical techniques: measurement of oxygen evolution potential (OER), cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and accelerated lifetime test (ALT). Higher oxygen overpotential, electrocatalytic specific area and service life were achieved with non-doped anode, while possible formation of nonconducting passivating layer and insufficient oxide layer compactness may have caused short service life of doped DSA anode. In comparison with other commercial DSA anodes, syntesised anodes are required to have longer service life for their potential application in industrial processing plants.

Keywords: DSA anodes, electrochemical oxidation, wastewater treatment, termochemical decomposition

INTRODUCTION

In electrochemical oxidation (EO)–a promising alternative for wastewater treatment, the oxidation of toxic, recalcitrant and bio-refractory pollutants can be achieved through direct electron transfer or indirect mediated oxidation in the bulk solution. Ti/SnO_2-Sb-type anodes as the most studied non-active anodes, represent the low cost and high overpotential anodes for the oxygen evolution reaction in which $^{\bullet}OH$ radicals are generated [1]. However, amount of $^{\bullet}OH$ radicals responsible for oxidation of toxic compounds is dependant upon the number of active sites on DSA anodes which is further affected by oxide layer composition and structure [2]. Ti/SnO_2-Sb-type anodes have proven as very efficient in electrochemical oxidation of highly toxic organic pollutants as p-chlorophenol, acid orange and perfluorooctanic acid [3–5]. Doping SnO_2 oxide layer with antimony, enhanced dielectric properties by forming essential oxygen vacancies [6,7]. Possitive effect of Mn doping on DSA service life was reported by Li *et al.* [2] and Massa *et al.* [8], while positive effect of Cr doping on crystallinity and grain size of oxide layer was previosly researched by Shao *et al.* [9].

EXPERIMENTAL

Titanium substrate (3.9 cm×1 cm×0.01 cm) was polished (grits 150 and 1500) in order to remove oxide layer and other surface impurities, washed by distilled water and degreased in ethanol for 10 minutes. Futher, metallic substrate was etched in 10% oxalic acid for 60 minutes at 85°C. Substrate was additionally washed by distilled water and dried at 105°C.

Precursor solutions were prepared by dissolving $SnCl_4 \cdot 5H_2O$ and Sb_2O_3 in 25 ml ethanol with addition of 2 ml conc. HCl. In one of those solutions, $CrCl_3 \cdot 6H_2O$ and $MnCl_2 \cdot 4H_2O$ were additionally added. The composition of precursor solutions is shown in Table 1.

Table 1 *Composition of precursor solutions*

Component	Mass (g)	
	Precursor 1	Precursor 2
$SnCl_4 \cdot 5H_2O$	5.6413	5.6413
Sb_2O_3	0.2186	0.2186
$CrCl_3 \cdot 6H_2O$	0.2665	/
$MnCl_2 \cdot 4H_2O$	0.2118	/

Prepared precursor solutions were then applied by brush until titanium substrate surface was fully covered. Substrate was dried at 105°C for 5 minutes, and heated in furnace at 550°C for 5 minutes. This proces was repeated 5 times with the final layer being calcined at 550°C for 1 hour. Substrate mass was measured throughout the whole process in order to determine the oxide loading, which is shown in Table 2.

Table 2 *Substrate mass througout preparation and oxide loading of synthesised anodes*

Anode	Substrate mass (g)			Mass DSA (g)	Oxide layer mass (g)	Oxide loading (mg/cm^2)
	Initial	After polishing	After etching			
DSA1	1.4713	1.4520	1.4040	1.4144	0.0104	1.23
DSA2	1.5160	1.4893	1.4140	1.4865	0.0725	7.97

For electrochemical testing of synthesised anodes, potentiostat (IVIUM XRE, IVIUM Technologies) was used, with the appropriate software. The surface redox behaviour of the coatings was characterized in 0.25 M aqueous Na_2SO_4 solution by cyclic voltammetry at 20 mV/s, 50 mV/s and 100 mV/s, with the electrode potential being scanned between 0 and 1 V. The oxygen evolution reaction (OER) was studied via linear voltammetry under potentiostatic control in the same electrolyte between 0.5 and 2.5 V. Applied scan rate was 10 mV/s. EIS measurements were conducted in same solution in the frequency range of 100 kHz–1 Hz. ALT test was conducted in 0.5M H_2SO_4, at constant current density of 500 mA/cm^2, until potential of 10 V was reached. All measurements were conducted at room temperature in naturally aerated solutions.

RESULTS AND DISCUSSION

OER potential values for DSA1 and DSA2, as a direct indicator of electrocatalytic activity of DSA anodes [10], were determined at the intersection point of the tangent and the horizontal line at 0 V potential shown in Figure 1.

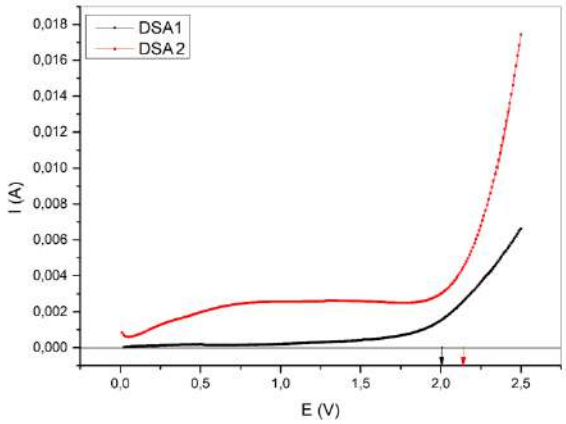

Figure 1 *Linear sweep voltammetry (LSV) of synthesized DSA anodes in 0.25 M* Na_2SO_4

Higher oxygen evolution potential (OEP) values are related to high electrocatalytic activity and better performance of anodes in electrochemical oxidation of recalcitrant organic compounds in water. Lower OEP values indicate shorter service life due to passivation of substrate and degradation of oxide layer; which would lead to higher consumption of electric energy in electrochemical oxidation [11]. OEP for DSA2 was estimated to be 2.14 V, while for DSA1 OEP was 2.01 V, which indicates that non-doped DSA2 anode has better catalytic properties. It is assumed that lower crystallinity, lower number of active sites and speciffic crystal structure could be the cause of lower OEP of DSA1 [12]. However, according to the estimated OEP values are considered to be relatively high and would indicate that synthesised anodes could be used for the processes of electrochemical oxidation [13].

Cyclic voltammetry curves shown in Figure 2, were obtained in potential range from 0 V to 1 V, considered to be optimal for determination of capacitivity in aqueous solutions.

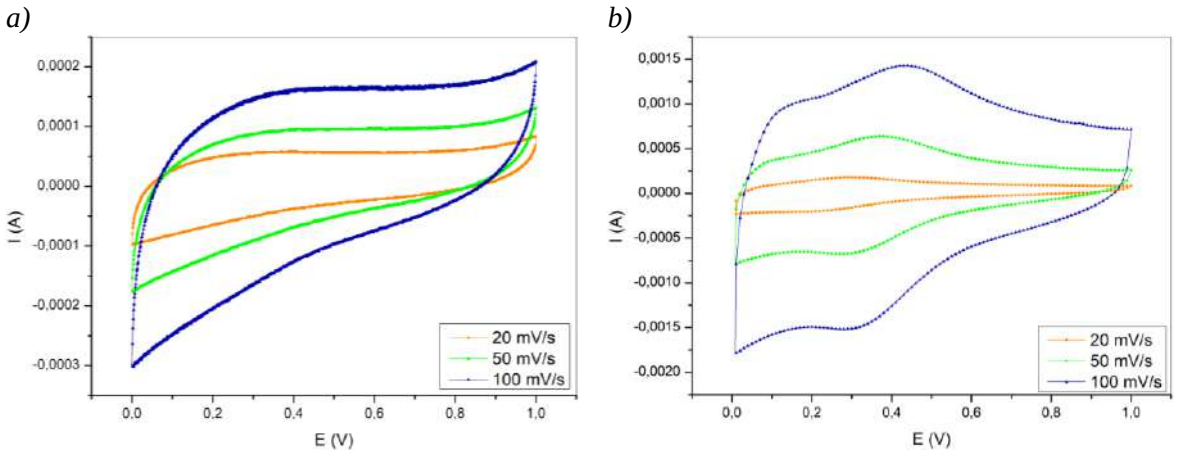

Figure 2 *Cyclic voltammetry curves for a) DSA1 and b) DSA2 anodes at different scan rates*

According to the CV plots shown in Figure 2, the decrease of cathodic current at potentials lower than 0.1 V indicates the reduction of SnO_2 might occur which could further cause degradation of oxide layer [14]. Voltammetric profiles indicate that capacitivity rises with the increase in scan rate, and that higher capacitivity is observed for DSA2 anode [15]. No noticable redox peaks were observed. However, the increase of current at potentials higher than 1.7 V due to intensified oxygen evolution. According to this phenomenon, synthesised anodes are considered non-active anodes [14]. Current peaks noticed at CV curves shown in Figure 2 b), are considered to be due to adsorption (0.4–0.45 V) and desorption (0.35 V) of sulfate ions on the surface of anode [16].

In order for roughness factor (R_f) and voltammetric charge (q*) to be determined and for additional investigation of catalytic activity, specific capacitivity (C_m) of synthesised anodes was calculated using the following equation [15]:

$$C_m = \frac{Q}{2 \cdot \Delta V \cdot m} \text{ (F/g)} \quad (1)$$

Here Q represents voltametric charge (C)–obtained by integrating the area of voltammetric profiles, ΔV is the potential range in which the curves are positioned and *m* is oxide layer mass. R_f of examined anodes was determined by dividing their calculated capacitivity (given in mF/cm^2) with the capacitivity of rutile type TiO_2 (approximately 60 $\mu F/cm^2$). The calculated parameters are summarized in Table 3.

Table 3 *Oxide layer capacitivity, roughness factor and voltammetric charge of synthesised DSA anodes*

Anode	Oxide loading (g)	Scan rate (mV/s)	C_m (F/g)	C (mF/cm^2)	R_f	q* (mC/cm^2)
DSA1	0.01	20	0.1999	0.2368	3.95	0.47
		50	0.1321	0.1565	2.61	0.31
		100	0.1160	0.1374	2.29	0.27
DSA2	0.07	20	0.0700	0.5584	9.31	1.12
		50	0.1065	0.8488	14.15	1.70
		100	0.1332	1.0624	17.71	2.12

Considering the results shown in Table 3, it can be concluded that DSA1 has less active sites on the oxide layer surface, and therfore being less effective than DSA2 anode in terms of electrocatalytic activity [17]. Main cause of larger electrocatalytic active area of DSA2 might be the formation of larger number of smaller-sized crystals [18].

EIS measurements were conducted according to the determined OEP values of syntesised anodes, at which the most dominant process is oxygen evolution. Fitting results were obtained via proposed equivalent circuit model shown in Figure 3.

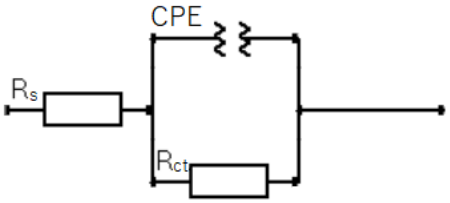

Figure 3 *Equivalent circuit model used for fitting EIS data*

In Figure 3, Randles' circuit model is composed of R_s-resistance of electrolyte solution, R_{ct}-charge transfer resistance during OER, and CPE which is a constant phase element that is usually used instead of a double layer capacitance to account for the non-ideal capacitive response of the interface [19]. Niquist plots for examined anodes are shown in Figure 4.

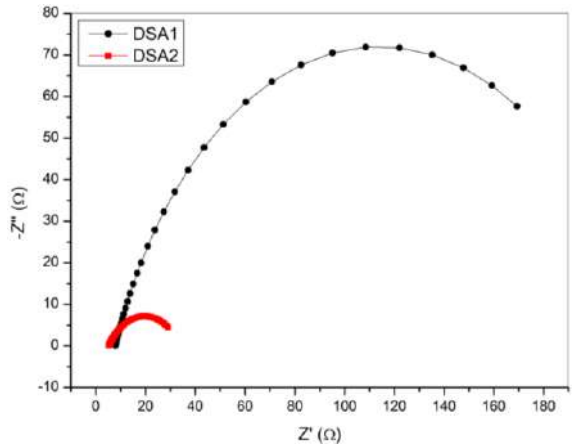

Figure 4 *Niquist plots for DSA1 and DSA2*

Speciffic shape of curves shown in Figure 4, is distinctive for anodes with pronounced roughness, synthesised by thermal decomposition method. The size of half-circle shaped curve is related to the charge transfer resistance, which further shows that better catalytic properties are observed for DSA2 anode [12]. Parameters of equivalent circuit were further determined, and are given in Table 4.

Table 4 *Equivalent circuit parameters*

Anode	R_s (Ω)	R_{ct} (Ω)	CPE	
			Q_{dl}	n
DSA1	7.89	$2.12 \cdot 10^{2}$	$4.79 \cdot 10^{-5}$	0.76
DSA2	5.18	28.8	$5.76 \cdot 10^{-5}$	0.58

It is assumed that higher charge transfer resistance reported for DSA1 anode, might be due to formation of low-conducting TiO_2 during the synthesis procedure or prolonged contact with electrolyte solution [20]. Relatively low n values for DSA1 and DSA2 indicate the existence highly porous and rough oxide layer surface [17]. Finally, ALT test was conducted to estimate real service life. In EO processes, it is desired for anode to have long service life

[20]. ALT test was conducted until potential of 10 V was reached, at which anodes were presumed to be deactivated. ALT test results are shown in Table 5.

Table 5 *ALT test results*

Anode	Service life (h)	Real service life (h) – at 100 mA/cm^2	Real service life (h) – at 10 mA/cm^2
DSA1	0.01	0.23	2.3
DSA2	0.64	16.1	161

Obtained ALT test results indicate that DSA2 anode has significantly longer real service life, while the low service life of DSA1 anode is considered to be the cause of formation of TiO_2 layer and degradation of oxide layer [21].

CONCLUSION

Linear potentiodynamic measurements confirmed that both DSA1 and DSA2 have relatively high OEP, further proving that the synthesised anodes have electrocatalytic properties. These anodes are considered to be a non-active DSA anode type, due to lack of redox peaks on cyclic voltammograms. Better catalytic properties were confirmed for non-doped DSA2 anode in terms of higher values of OEP, capacitivity, voltametric charge and roughness factor. This indicates that intensified hydroxyl radical formation would lead to more effective electrochemical oxidation of organic compounds. Relatively fast deactivation of DSA1 is considered to be due to passivation of substrate and erosion of oxide layer.

ACKNOWLEDGEMENT

The authors would like to acknowledge financial support from Ministry of Education, Science and Technological development of the Republic of Serbia (Agreement No 451-03-68/2022-14/200131).

REFERENCES

[1] G.O.S. Santos, A.R. Dória, V.M. Vasconcelos, *et al.*, Chemosphere; 259 (2020).

[2] D. Li, J. Tang, X. Zhou, *et al*., Chemosphere; 149 (2016) 49–56.

[3] F. Cao, J. Tan, S. Zhang, *et al*., J. Chem; (2021) 1–13.

[4] H. Lin, J. Niu, S. Ding, *et al*., Water Res; 46 (7) (2012) 2281–2289.

[5] Y. Duan, Y. Chen, Q. Wen, *et al*., J. Electroanal. Chem; 768 (2016) 81–88.

[6] A. Chen, X. Zhu, J. Xi, *et al*., J. Alloys Compd; 683 (2016) 501–505.

[7] C. Carlesi Jara, G.R. Salazar-Banda, R.S. Arratia, *et al*., Chem. Eng. J; 171 (2011) 1253–1262.

[8] A. Massa, S. Hernández, A. Lamberti, *et al*., Appl. Catal. B; 203 (2017) 270–281.

[9] C. Shao, F. Zhang, X. Li, *et al*., J. Electroanal. Chem; 832 (2019) 436–443.

[10] L. Li, Z. Huang, X. Fan, *et al*., Electrochim. Acta; 231 (2017) 354–362.

[11] G. Zhao, X. Cui, M. Liu, *et al*., ES&T; 43 (2009) 1480–1486.

[12] L.M. da Silva, G. de Oliveira Santiago Santos, M.M. de Salles Pupo, *et al*., J. Electroanal. Chem; 813 (2018) 127–133.

[13] H. Shekarchizade, M.K. Amini, Int. J. Electrochem; (2011) 1–13.

[14] L. Xu, M. Li, W. Xu, Electrochim. Acta; 166 (2015) 64–72.

[15] S.M. Chen, R. Ramachandran, V. Mani, *et al*., Int. J. Electrochem. Sci; 9 (2014) 4072–4085.

[16] A. Chen, S. Nigro, J. Phys. Chem. B; 107 (2003) 13341–13348.

[17] V.M. Vasconcelos, I.M.D. Gonzaga, A.R. Dória, *et al*., Electrochim. Acta; 364 (2020) 137273

[18] G.O.S. Santos, L. R. A. Silva, Y.G.S. Alves, *et al*., Chem. Eng. J; 355 (2019) 439–447.

[19] W. Choi, J. H. Choi, H. Park, Chem. Eng. J; 409 (2021).

[20] Q. Bi, W. Guan, Y. Gao, *et al.*, Electrochim. Acta; 306 (2019) 667–679.

[21] L. Xu, Y. Wang, W. Zhang, RSC Advances; 9 (67) (2019) 39242–39251.

tfbor.bg.ac.rs
eco.tfbor.bg.ac.rs

EcoTER'22

ISBN 978-86-6305-123-2