

**Second Regional Symposium  
on Electrochemistry  
South-East Europe**

**PROCEEDINGS**



**Belgrade, Serbia, June 6-10, 2010.**

CIP - Каталогизacija у публикацији  
Народна библиотека Србије, Београд

621.357/.359(082)(0.034.2)

541.1(082)(0.034.2)

620.193/.197(082)(0.034.2)

66.087(082)(0.034.2)

543.25(082)(0.034.2)

REGIONAL Symposium on Electrochemistry South-East Europe  
(2 ; 2010 ; Beograd) Proceedings [Elektronski izvor] / Second  
Regional Symposium on Electrochemistry South-East Europe,  
RSE-SEE, Belgrade, Serbia, June 6-10, 2010. ; [editors Branislav  
Nikolić, Vesna Mišković-Stanković, Aleksandar Dekanski]. – Belgrade :  
Serbian Chemical Society, 2010 (Belgrade : Serbian Chemical Society).  
- 1 elektronski optički disk (CD-ROM) : tekst ; 12 cm

Sistemski zahtevi: Nisu navedeni. - Nasl. sa naslovnog ekrana. –  
Tiraž 270. - Bibliografija uz svaki rad.

ISBN 978-86-7132-044-3

a) Електрохемијско инжењерство - Апстракти b) Галванотехника –  
Апстракти c) Електрохемија – Апстракти d) Електрохемијске  
реакције - Апстракти e) Антикорозиона заштита - Апстракти  
f) Аналитичка електрохемија - Апстракти  
COBISS.SR-ID 175354892

## ***Second Regional Symposium on Electrochemistry : : South-East Europe***

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### **PROCEEDINGS**

Published by

**Serbian Chemical Society**, Karnegijeva 4/III, PAK 135804, 11120 Belgrade, **SERBIA**  
phone./fax: +381 11 3370 467; [www.shd.org.rs](http://www.shd.org.rs), E-mail: [Office@shd.org.rs](mailto:Office@shd.org.rs)

For Publisher

**Ivanka POPOVIĆ**, *President of the Society*

Editors

**Branislav NIKOLIĆ**

**Vesna MIŠKOVIĆ-STANKOVIĆ**

**Aleksandar DEKANSKI**

Cover Design, Page Making and Computer Layout

**Aleksandar DEKANSKI**

Circulation:

**270 Copy Printing**

ISBN **978-86-7132-044-3**

Copying

**Serbian Chemical Society** - Karnegijeva 4/III, Belgrade, **SERBIA**

## Ethanol oxidation at Pt-based alloys and UPD modified Pt/C catalysts

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### Abstract

Activity of two alloys, Pt<sub>3</sub>Sn/C and Pt<sub>3</sub>Ru<sub>2</sub>/C, was compared with the activity of Pt/C modified with corresponding amounts of Sn<sub>UPD</sub> (~25 %) and Ru<sub>UPD</sub> (~40 %) in overall oxidation of ethanol. Pt<sub>3</sub>Sn/C, Pt<sub>3</sub>Ru<sub>2</sub>/C and Pt/C catalysts were characterized by XRD. To establish the activity and stability of the catalysts potentiodynamic, quasi steady-state and chronoamperometric measurements were performed. Both alloys are more active than Sn<sub>UPD</sub> or Ru<sub>UPD</sub> modified Pt/C catalysts. Electronic effect determining dominantly the activity of Pt<sub>3</sub>Sn/C is the main reason for its higher activity compared to Pt<sub>3</sub>Ru<sub>2</sub>/C. Since Sn<sub>UPD</sub> and Ru<sub>UPD</sub> do not provoke any significant modification of electronic environment, both modified Pt/C catalysts are less active than corresponding alloys. More pronounced difference in activity between Pt<sub>3</sub>Sn/C and Sn<sub>UPD</sub> modified Pt/C than between Pt<sub>3</sub>Ru<sub>2</sub>/C and Ru<sub>UPD</sub> modified Pt/C is caused by electronic effect in Pt<sub>3</sub>Sn/C. High activity of Pt<sub>3</sub>Sn/C modified with small amount of Sn<sub>UPD</sub> (~10%) can be explained by combining the electronic effect, causing less strongly bonded adsorbate on Pt sites and easier mobility of Sn<sub>UPD</sub>, with enhanced amount of oxygen-containing species on Sn sites resulting finally in reinforcement of bifunctional mechanism.

### Introduction

Ethanol is promising fuel for direct alcohol low temperature fuel cells due to its low toxicity, high energy density, mass production from renewable sources and easy storage and transportation. However, the lack of an efficient and selective anode catalyst able to break C-C bond providing complete oxidation to CO<sub>2</sub> with exchange of 12 e<sup>-</sup> per molecule and to oxidize adsorbed fragments produced by ethanol dissociation, is at present the main problem for a practical use of ethanol in DEFC.

Despite of fact that platinum is generally known as one of the best electrocatalyst for alcohol oxidation at low temperatures, it is limited capable for C-C bond scission and easily poisoned by CO and other carbonaceous intermediates.<sup>1</sup> To improve its electrocatalytic activity, especially at potentials of technical interest ( $E < 0.6$  V vs. RHE), Pt is modified by addition of transition metals providing oxygen-containing species at low potentials and facilitate the oxidative removal of poisoning species through bifunctional mechanism<sup>6</sup>. Addition of the second metal to platinum (by underpotential deposition or alloying) creates the bimetallic catalysts and changes the electronic and structural properties of the based material influencing its catalytic properties. It also alters the number of large Pt ensembles on platinum surfaces, which are important for the site demanding process such as C-C bond cleavage. All these effects influence the ethanol oxidation on bimetallic catalyst.

Among the other bimetallic catalysts PtSn/C and PtRu/C catalysts demonstrated the best performance in ethanol oxidation.

In this work ethanol oxidation was studied at two alloys, Pt<sub>3</sub>Sn/C and Pt<sub>3</sub>Ru<sub>2</sub>/C, as well as on Pt/C catalyst modified with the corresponding amounts of Sn<sub>UPD</sub> (25 %) and Ru<sub>UPD</sub> (40 %). Comparative investigation based on the effects influencing the catalytic properties of these electrodes enables better understanding of different activities between alloys, as well as between alloys and Pt/C modified by underpotential deposited Sn and Ru. This approach, which to our knowledge has not been used so far, resulted finally in comprehension of the superior activity of the catalyst created by modification of Pt<sub>3</sub>Sn/C with small amount of Sn<sub>UPD</sub> (~ 10%). It should be pointed out that this work deals with the activity of the catalysts in overall ethanol oxidation but not with their selectivity.

### Experimental

#### *Electrode preparation*

A commercially available Pt based catalysts provided by E-Tek, 20 wt% Pt<sub>3</sub>Sn alloy and by Tanaka Precious Metals Group (Kikinzoku International K.K), 47.5 wt% Pt and 33.5 wt% Pt<sub>3</sub>Ru<sub>2</sub> alloy, supported on high surface area carbon were used. The catalysts were applied to a glassy carbon substrate in the form of a thin-film.<sup>9</sup>**Error! Bookmark not defined.**

To avoid the contribution of any other anions Sn or Ru adlayers were prepared by holding the freshly prepared electrodes at -0.2 V in 0.1 M HClO<sub>4</sub> solution containing Sn or Ru ions, generated by

dissolving of Sn or Ru from the alloy matrix during cycling (20 cycles) of Pt<sub>3</sub>Sn/C and Pt<sub>3</sub>Ru<sub>2</sub>/C electrodes up to 0.70 V or 1.10 V, respectively. The Sn or Ru modified electrode was then rinsed with water and transferred to electrochemical cell.

### Characterization of the catalysts

The Pt/C, Pt<sub>3</sub>Ru<sub>2</sub>/C and Pt<sub>3</sub>Sn/C catalysts were characterized by X-ray diffraction (Table 1).

Catalysts	Nominal content (Pt:Me)	Mean crystallite diameter (nm)	Lattice parameter (nm)	Atomic fraction $X_M$	$M_{\text{alloy}}$ (%)
47.5 wt% Pt/C		3.9	0.39166		
33.5 wt% Pt <sub>3</sub> Ru <sub>2</sub> /C	60:40	4.5	0.3871	0.368	87.4
20 wt% Pt <sub>3</sub> Sn/C	75:25	5.2	0.398385	0.243	96.4

## Results and discussion

Ethanol oxidation at Pt<sub>3</sub>Sn/C, Pt/C and Sn<sub>UPD</sub> modified Pt/C and Pt<sub>3</sub>Sn/C catalysts are displayed in Fig. 1.

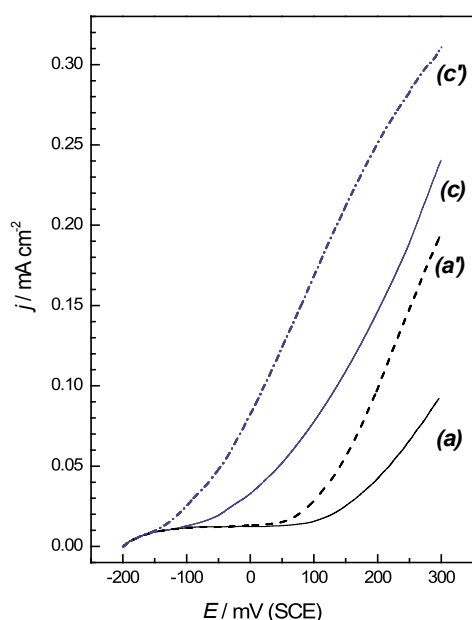


Fig. 1. Potentiodynamic curves for the oxidation of 0.5 M C<sub>2</sub>H<sub>5</sub>OH in 0.1 M HClO<sub>4</sub> at Pt/C (curve a), at Pt/C modified with 25% Sn<sub>UPD</sub> (curve a'), at Pt<sub>3</sub>Sn/C (curve c) and at Pt<sub>3</sub>Sn/C modified with 10% Sn<sub>UPD</sub> (curve c').  $v = 20 \text{ mV s}^{-1}$ .

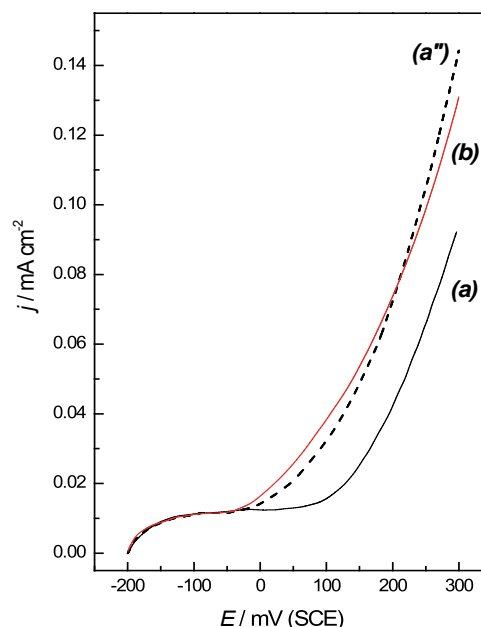


Fig. 2. Potentiodynamic curves for the oxidation of 0.5 M C<sub>2</sub>H<sub>5</sub>OH in 0.1 M HClO<sub>4</sub> at Pt/C (curve a), at Pt/C modified with 40% Ru<sub>UPD</sub> (curve a'') and at Pt<sub>3</sub>Ru<sub>2</sub>/C (curve b).  $v = 20 \text{ mV s}^{-1}$ .

The activity of Pt/C catalyst is improved by Sn<sub>UPD</sub> layer. The reaction commences at  $\sim 0.0$  V (curve a'), i.e. at  $\sim 0.1$  V less positive potentials relative to Pt/C (curve a).

Comparison of Pt<sub>3</sub>Sn/C containing  $\sim 25$  at% of Sn (curve c) with Pt/C modified by the same amount of Sn<sub>UPD</sub> (curve a') reveals clearly that the alloy is considerably more active. The onset of the reaction at Pt<sub>3</sub>Sn/C is shifted for more than 0.1 V to less positive potentials and the current densities are enhanced. Spectroscopic analysis of Sn<sub>UPD</sub> on Pt/C shows that Sn<sub>UPD</sub> interacts with oxygen species similar as in Pt<sub>3</sub>Sn/C alloy, but underpotential deposition of Sn on Pt/C induces much less electronic changes in Pt/C than in Pt<sub>3</sub>Sn/C.<sup>14</sup> It means that Sn<sub>UPD</sub> does not interfere remarkably with ability of Pt to adsorb strongly ethanol or the adsorbate generated by ethanol dissociation, which should be the main reason for the lower activity of Sn<sub>UPD</sub> modified Pt/C in respect to Pt<sub>3</sub>Sn/C.

Small amount of Sn ( $\sim 10$  %) electrodeposited on Pt<sub>3</sub>Sn/C promotes the activity of alloy (curve c') creating powerful catalyst for ethanol oxidation as it was shown in Ref.<sup>15</sup>. High activity of this catalyst can be explained by combining the electronic effect, causing less strongly bonded adsorbate on Pt sites and easier mobility of Sn<sub>ad</sub>,<sup>16</sup> with enhanced amount of oxygen-containing species on Sn sites resulting, as final consequence, in reinforcement of bifunctional mechanism.

Using the same approach ethanol oxidation was examined at  $\text{Pt}_3\text{Ru}_2/\text{C}$  containing 40% of Ru (Fig. 2) and compared with Pt/C catalyst modified with approximately the same amount ( $\sim 40\%$ ) of  $\text{Ru}_{\text{UPD}}$ , (curves *b* and *a''*, respectively).

Inspection of the results given in Fig. 2 shows the significant difference regarding to the corresponding results obtained at  $\text{Pt}_3\text{Sn}/\text{C}$  and  $\text{Sn}_{\text{UPD}}$  modified Pt/C catalysts (Fig. 1). The substantial contrast easily recognized is a small difference between activity of  $\text{Pt}_3\text{Ru}_2/\text{C}$  (curve *b*) and to the Pt/C modified by the same amount underpotential deposited Ru (curve *a''*). This is a reliable proof that electronic or structural effects do not provoke significant influence on the activity of Ru alloyed Pt catalysts. In that context the high alloying degree of 87.4% (Table 1) is not as relevant for an estimation of the catalytic properties of  $\text{Pt}_3\text{Ru}_2/\text{C}$  as it is in a case of  $\text{Pt}_3\text{Sn}/\text{C}$  catalyst. Since underpotential deposited of Ru on Pt/C does not provoke significant electronic changes in Pt/C<sup>17,18</sup> ethanol oxidation on respective catalysts obeys the conditions relevant for the bifunctional mechanism. In that sense, the ratio between Pt sites, which adsorb ethanol and Ru sites which nucleate oxygen species to oxidize that adsorbate, becomes crucial. The ratio Pt/Ru = 60:40 fulfilled in  $\text{Pt}_3\text{Ru}_2/\text{C}$  as well as in Pt/C modified by 40% of  $\text{Ru}_{\text{UPD}}$  provide the best catalytic performance.<sup>19</sup>

The activity of the catalysts studied in ethanol oxidation obtained under quasi steady state condition is given in Figs. 3 and 4. The  $\text{Pt}_3\text{Sn}/\text{C}$  is more active than Pt/C modified by  $\text{Sn}_{\text{UPD}}$  ( $\sim 25\%$ ) catalysts (Fig. 3) and considerably more active than Pt/C. The activity of  $\text{Pt}_3\text{Ru}_2/\text{C}$  and Pt/C modified by  $\text{Ru}_{\text{UPD}}$  ( $\sim 40\%$ ) are similar, but both catalysts are more active than Pt/C (Fig. 4).  $\text{Pt}_3\text{Sn}/\text{C}$  modified by  $\sim 10\%$   $\text{Sn}_{\text{UPD}}$  is the best catalyst studied.

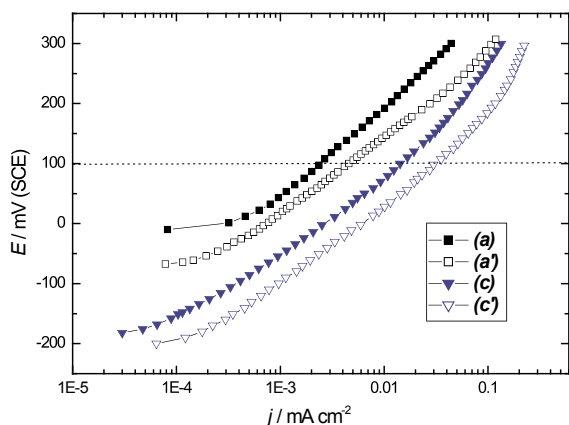


Fig. 3. Tafel plots for oxidation of 0.5 M  $\text{C}_2\text{H}_5\text{OH}$  in 0.1 M  $\text{HClO}_4$  solution at: Pt/C (curve *a*), Pt/C modified with 25%  $\text{Sn}_{\text{UPD}}$  (curve *a'*),  $\text{Pt}_3\text{Sn}/\text{C}$  (curve *c*) and  $\text{Pt}_3\text{Sn}/\text{C}$  modified with 10%  $\text{Sn}_{\text{UPD}}$  (curve *c'*).  $\nu = 1 \text{ mV s}^{-1}$ .

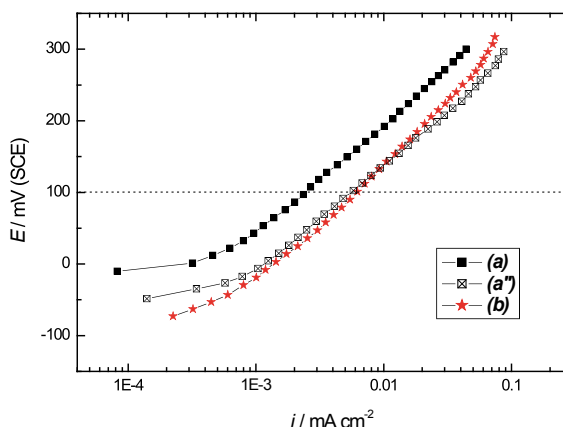


Fig. 4. Tafel plots for oxidation of 0.5 M  $\text{C}_2\text{H}_5\text{OH}$  in 0.1 M  $\text{HClO}_4$  solution at: Pt/C (curve *a*), Pt/C modified with 40%  $\text{Ru}_{\text{UPD}}$  (curve *a''*) and  $\text{Pt}_3\text{Ru}_2/\text{C}$  (curve *b*).  $\nu = 1 \text{ mV s}^{-1}$ .

## Conclusions

According to the results obtained in this work dealing with the effects influencing the overall ethanol oxidation on the catalysts studied the following conclusions can be pointed out:

- $\text{Pt}_3\text{Sn}/\text{C}$  is more active than  $\text{Pt}_3\text{Ru}_2/\text{C}$  or corresponding  $\text{Sn}_{\text{UPD}}$  or  $\text{Ru}_{\text{UPD}}$  modified Pt/C catalysts as revealed from potentiodynamic and quasi steady state measurements. Its high activity originates mainly from the electronic effect causing the weak bonded adsorbate generated by ethanol adsorption on Pt sites, and appropriate amount of oxygen-containing species, labile bounded to Sn, to oxidize adsorbate through the bifunctional mechanism.
- Regardless whether electronic effect exists or not in  $\text{Pt}_3\text{Ru}_2/\text{C}$  the bond between Pt and adsorbate remains strong and that is the main reason for its lower activity than  $\text{Pt}_3\text{Sn}/\text{C}$  although Ru is capable as well as Sn to dissociate water at low potentials.
- Since underpotential deposition of Sn or Ru does not provoke any significant electronic effect both modified Pt/C catalysts are less active than corresponding alloys. Accordingly, more pronounced difference between  $\text{Pt}_3\text{Sn}/\text{C}$  and  $\text{Sn}_{\text{UPD}}$  modified Pt/C (25% Sn) than between  $\text{Pt}_3\text{Ru}_2/\text{C}$  and  $\text{Ru}_{\text{UPD}}$  modified Pt/C (40% Ru) is caused by electronic effect in  $\text{Pt}_3\text{Sn}/\text{C}$ .
- Modification of  $\text{Pt}_3\text{Sn}/\text{C}$  with a small amount of  $\text{Sn}_{\text{UPD}}$  ( $\sim 10\%$ ) creates powerful catalyst for overall ethanol oxidation.

*Acknowledgement: This work was financially supported by the Ministry of Science and Technological Development, Republic of Serbia, Contract No. H-142056.*

## References

1. G.A. Camara, T. Iwasita, *J. Electroanal. Chem.*, **578** (2005) 315.
2. H. Wang, Z. Jusys, R.J. Behm, *J. Phys. Chem. B*, **108** (2004) 19413.
3. M.H. Shao, R.R. Adžić, *Electrochim. Acta*, **50** (2005) 2415.
4. C. Coutanceau, S. Brimaud, C. Lamy, J.-M. Leger, L. Dubau, S. Rousseau, F. Vigier, *Electrochim. Acta*, **53** (2008) 6865.
5. S.C.S. Lai, E.F. Kleyne, V. Rosca, M.T. Koper, *J. Phys. Chem. C*, **112** (2008) 19080.
6. M. Watanabe, S. Motoo, *J. Electroanal. Chem.*, **60** (1975) 267.
7. H. Wang, Z. Jusys, R.J. Behm, *J. Power Sources*, **154** (2006) 351.
8. L. Colmenares, H. Wang, Z. Jusys, L. Jiang, S. Yan, G.Q. Sun, R.J. Behm, *Electrochim. Acta*, **52** (2006) 221.
9. Q. Wang, G.Q. Sun, L.H. Jiang, Q. Xin, S.G. Sun, Y.X. Jiang, S.P. Chen, Z. Jusys, R.J. Behm, *Phys. Chem. Chem. Phys.*, **9** (2007) 2686.
10. F.C. Simoes, D.M. dosAnjos, F. Vigier, J.-M. Leger, F. Hahn, C. Coutanceau, E.R. Gonzalez, G. Tremiliosi-Filho, A.R. deAndrade, P. Olivi, K.B. Kokoh, *J. Power Sources*, **167** (2007) 1.
11. S. Delime, J.-M. Leger, C. Lamy, *J. Appl. Electrochem.*, **29** (1999) 1249.
12. J.-M. Leger, S. Rousseau, C. Coutanceau, F. Hahn, C. Lamy, *Electrochim. Acta*, **50** (2005) 5118.
13. W.J. Zhou, Z.H. Zhou, S.Q. Song, W.Z. Li, G.Q. Sun, P. Tsiakaras, Q. Xin, *Appl. Catal. B: Environmental*, **46** (2003) 273.
14. S. Mukerjee, J. McBreen, *J. Electrochem. Soc.*, **146** (1999) 600.
15. A.V. Tripković, K.Dj. Popović, J.D. Lović, V.M. Jovanović, S.I. Stevanović, D.V. Tripković, *Electrochem. Commun.*, **11** (2009) 1030.
16. Y. Yao, Q. Fu, Z. Zhang, H. Zhang, T. Ma, D. Tan, X. Bao, *Appl. Surf. Sci.* **254** (2008) 3808.
17. A.K. Shukla, A.S. Arico, K.M. El-Khatib, H. Kim, P.L. Antonucci, V. Antonucci, *App. Surf. Sci.*, **137** (1999) 20.
18. S. Mukerjee, J. McBreen, 2<sup>nd</sup> International Sump. on New Materials for Fuel Cells and Modern Battery Systems, in: O. Savadoga, P.R. Roberge (Eds.), Montreal, Canada, 1997, p. 548.
19. G.A. Camara, R.B. de Lima, T. Iwasita, *Electrochem. Commun.*, **6** (2004) 812.