Electrochemistry Communications 11 (2009) 1030–1033

Contents lists available at ScienceDirect

Electrochemistry Communications

journal homepage: www.elsevier.com/locate/elecom

Promotional effect of Sn_{ad} on the ethanol oxidation at Pt_3Sn/C catalyst

A.V. Tripković [a,*], K.Dj. Popović [a], J.D. Lović [a], V.M. Jovanović [a], S.I. Stevanović [a], D.V. Tripković [a], A. Kowal [b]

[a] ICTM-Institute of Electrochemistry, University of Belgrade, Njegoševa 12, P.O. Box 473, 11000 Belgrade, Serbia
[b] Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences, Krakow, Niezapominajek 8, 30-239, Poland

ARTICLE INFO

Article history:
Received 2 February 2009
Received in revised form 21 February 2009
Accepted 3 March 2009
Available online 10 March 2009

Keywords:
Ethanol oxidation
Sn adlayer
Pt_3Sn/C
Pt/C
XRD

ABSTRACT

Oxidation of ethanol was studied at Sn_{ad} modified and unmodified Pt_3Sn/C and Pt/C catalysts. Pt_3Sn/C and Pt/C catalysts were characterized by XRD. Potentiodynamic and chronoamperometric measurements were used to establish catalytic activity and stability. High activity achieved at Sn_{ad} modified Pt_3Sn/C catalyst has not been observed at any bimetallic catalyst so far. Promotional effect of Sn_{ad} on the ethanol oxidation was related to the enhancement of CO oxidation rate in bifunctional mechanism. It was shown that electrodeposited Sn exhibited different effect on the catalytic activity compared to Sn in alloy.

1. Introduction

Ethanol with its high energy density, likely production from renewable sources and easy storage and transportation is almost an ideal fuel for fuel cells. However, at present a lack of sufficiently active and selective anode electrocatalyst which can provide complete ethanol oxidation to CO_2 is the main problem for its practical use in direct ethanol fuel cells (DEFC). Partial oxidation of ethanol generating acetaldehyde and acetic acid prevails over complete oxidation to CO_2 on platinum as well as on platinum based bimetallic catalysts detected by means of FTIR and DEMS [1–5]. The adsorbate formed by dehydrogenation of ethanol consists of $C_{1,ad}$ mostly CO_{ad} [6,7] and CH [8] fragments generated by splitting of C–C bond and different $C_{2,ad}$ species with the intact C–C bond [3,9].

The oxidation of adsorbed C_1 fragments to CO_2 as well as adsorbed C_2 species to acetic acid requires OH_{ad}. The presence of transition metals, such as Sn, in Pt based catalysts promotes ethanol oxidation by adsorption of OH species at considerably lower potentials compared to Pt permitting bifunctional mechanism to proceed [10]. Besides, electronic effect based on the influence of the transition metals on the neighboring Pt atoms leading to the weaker bond of any adsorbed species was proposed as reason for enhanced activity of bimetallic catalysts [11].

In this work ethanol oxidation was studied at unmodified and Sn_{ad} modified Pt_3Sn/C and Pt/C catalysts in order to establish the difference between the effects of electrodeposited Sn and Sn in alloy. This approach has not been applied on high area carbon-supported catalysts so far.

2. Experimental

The high area carbon supported platinum–tin (Pt_3Sn/C) and platinum (Pt/C) nanocatalysts with 20 wt% alloy and 47.5 wt% Pt (E-Tek and Tanaka Precious Metal Group) were applied to a glassy carbon substrate in the form of a thin-film. A homogenous catalyst layer was prepared according to procedure described elsewhere [12]. The resulting metal loading was $25\ \mu g\ cm^{-2}$.

To avoid the contribution of any other anions Sn adlayer was prepared by holding the electrodes at −0.2 V for 120 s in 0.1 M $HClO_4$ containing Sn ions, produced by dissolving of Sn from the alloy matrix during cycling of Pt_3Sn/C electrode between −0.25 V and 0.70 V (20 cycles at $50\ mV\ s^{-1}$). The Sn modified electrode was then rinsed with water and transferred to electrochemical cell.

The Pt/C and Pt_3Sn/C catalysts were characterized by X-ray diffraction. XRD measurements were carried out with a Siemens D5005 (Bruker-AXS) diffractometer using Cu Kα source operating at 40 mA and 40 kV and a graphite monochromator. The quantitative analysis of phase content and crystalline size calculations were carried out by multiphase Rietveld refinement using Topas software and Fundamental Parameters approach for the modeling of peak shape.

Electrochemical measurements were carried out at room temperature in nitrogen purged 0.1 M $HClO_4$ solution in a standard three compartment electrochemical cell with a Pt wire as the counter electrode and a saturated calomel electrode (SCE) as the reference. The reagents used were of p.a. purity and solutions were

---

* Corresponding author. Tel.: +381 11 3370390; fax: ++381 11 3370389.
E-mail addresses: amalija@tmf.bg.ac.rs, amalija@elab.tmf.bg.ac.yu (A.V. Tripković).

1388-2481/$ - see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.elecom.2009.03.004

prepared with high purity water. Ethanol was added in the solution while holding the electrode potential at −0.2 V. The catalytic activity was measured using the potentiodynamic (sweep rate 20 mV s^{-1}) and chronoamperometric methods. The current-time transient curves were recorded during 30 min upon the immersion of the electrode in the solution at −0.2 V for 2 s prior to stepping to 0.2 V.

Current densities are expressed as mA mg^{-1}, because establishing the active surface area of the catalysts from the CO stripping is not accurate due to Sn dissolution occurring parallel to the CO oxidation. The potentials are given *versus* SCE.

The VoltaLab PGZ402 (Radiometer Analytical) was used in electrochemical experiments.

3. Results and discussion

Fig. 1 shows the XRD patterns of the carbon-supported Pt and Pt_3Sn catalysts. Two phases were identified in both patterns, one with the main characteristic peaks of *fcc* platinum crystalline structure (111, 200, 220 and 311) and another with diffraction peak at around 25° related to hexagonal structure of Vulcan XC-72R carbon support. The diffraction peaks of the Pt_3Sn/C catalyst are shifted to lower 2θ values with respect to the corresponding peaks at Pt/C as a consequence of alloy formation between Pt and Sn. No peaks for Sn or Pt oxides were found. However, it does not mean that they are not present in undetectable small amounts or in amorphous form.

Quantitative analysis based on Rietveld calculation gave 17 wt% for Pt_3Sn and 83 wt% for carbon, which is in a good agreement with nominal phase content.

The lattice parameters calculated from (220) peak positions are 3.9838(5) Å and 3.916(6) Å for Pt_3Sn/C and Pt/C catalysts, respectively. The lattice parameter for the Pt_3Sn/C catalyst is larger due to a lattice expansion caused by incorporation of bigger Sn atom in the *fcc* structure of platinum [13]. The value of the lattice parameter for this catalyst is close to the value of 4.0005 Å [14] indicating a high degree of alloying [3,15]. Based on combined XRD and ICP–AES [15], as well as EDX and XPS [3] analysis of surface composition of Pt–Sn catalysts with similarly high alloying degree, it could be assumed that the surface of our Pt_3Sn/C catalyst is Pt rich.

The average particle sizes for Pt/C and Pt_3Sn/C catalysts are 3.9 nm and 5.2 nm, respectively. Upon Sn_{ad} modification of both catalysts the average particle size should not be changed significantly [16].

Basic voltammograms of unmodified and Sn_{ad} modified Pt_3Sn/C and Pt/C catalysts are displayed in Fig. 2. The decrease of charge in hydrogen region of ~10% between unmodified and Sn_{ad} modified Pt_3Sn/C catalyst (Fig. 2a) could be related to the coverage with Sn_{ad} at Pt_3Sn/C, assuming that hydrogen does not adsorb on Sn [17]. The similar coverage with Sn_{ad} was observed in the case of modified Pt/C catalyst (Fig. 2b).

Ethanol oxidation on Pt/C, Pt_3Sn/C and on Sn_{ad} modified catalysts in acid solution is presented in Fig. 3. The positive potentials are limited to 0.3 V to avoid any Sn dissolution.

Pt/C catalyst (curve a) exhibits a low activity. Ethanol oxidation commences at ~0.1 V when dissociative adsorption of water occurs providing OH_{ad} [18] needed for oxidation of adsorbate containing C_1 and C_2 species produced by dissociative adsorption of ethanol.

Pt_3Sn/C catalyst is highly active in ethanol oxidation with the onset potential of −0.15 V (shifted for 0.25 V towards more negative potentials compared to Pt/C) and rapid kinetics (curve b), which is in accordance with the relevant results in the literature in the potential range of technical interest, i.e. at $E < 0.6$ V (RHE) [12].

The activity of Pt/C and Pt_3Sn/C catalyst is significantly improved by Sn_{ad} layer (curves a′ and b′). The onset potential is shifted for ~0.05 V towards more negative potentials and the current densities in the whole potential region studied are two times higher relative to unmodified catalysts.

Sn adatoms tend to nucleate on the particle edges due to their high mobility and low surface energy [19,20]. As the coverage with Sn_{ad} is low, ~10% (Fig. 2), it is reasonable to assume that Sn is

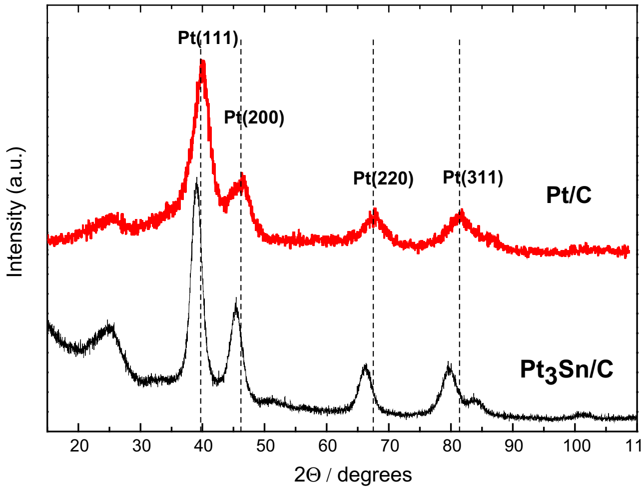

Fig. 1. XRD patterns of Pt_3Sn/C and Pt/C catalysts. Vertical lines represent position of peaks of pure Pt.

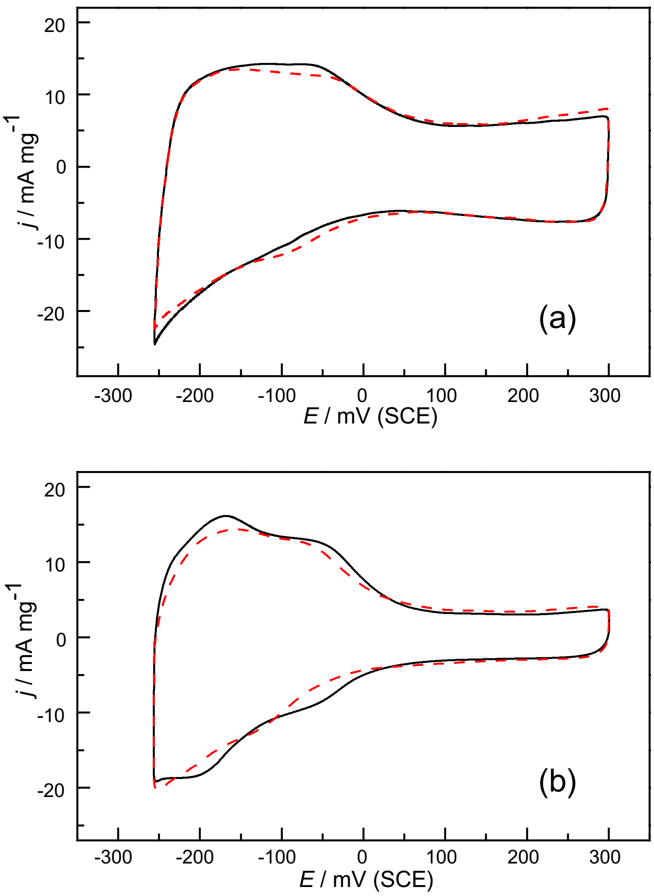

Fig. 2. Basic voltammograms of unmodified (——) and Sn_{ad} modified (- - -) Pt_3Sn/C (a) and Pt/C (b) electrode in 0.1 M $HClO_4$ solution $v = 20$ mV s^{-1}.