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Impact of deposition conditions on the electrocatalytic performances of Sn-Pd catalysts in ethanol oxidation reaction

Uticaj uslova taloženja na elektrohemijske performanse Sn-Pd katalizatora u reakciji oksidacije etanola

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Abstract

We are reporting the electrochemical behavior of bimetallic Sn-Pd catalysts in ethanol oxidation reaction (EOR). Sn-Pd catalysts were prepared by two step electrodeposition technique whereby by regulating deposition conditions various forms of Sn dendrites and different atomic ratios of Sn:Pd were achieved. The electrocatalytic activity of Sn-Pd catalysts were evaluated for EOR in alkaline solution using cyclic voltammetry (CV) and chronoamperometric (CA) measurements. The highest activity and anti-poisoning ability exhibited $Sn_{0.67}$-$Pd_{0.33}$ catalyst due to the better utilization of Pd. At $Sn_{0.67}$-$Pd_{0.33}$ catalyst Sn better contribute Pd to oxidize chemisorbed species by providing adsorbed OH^- species, thereby enabling well synergy of Sn with Pd.
Keywords: *electrodeposition; electrocatalysts; electrooxidation; dendrites.*

Izvod

U ovom radu se bavimo ispitivanjem elektrohemijskog ponašanja Sn-Pd katalizatora u reakciji oksidacije etanola (ROE). Sn-Pd katalizatori su dobijeni dvostepenim elektrohemijskim taloženjem, pri čemu se regulisanjem uslova taloženja dobijaju različite forme Sn dendrita i različiti atomski odnosi Sn:Pd. Elektrohemijska aktivnost Sn-Pd katalizatora je procenjena u ROE u alkalnoj sredini korišćenjem cilične voltametrije (CV) i hronoamperometrijskim merenjima. Najveću aktivnost i toleranciju prema otrovima je pokazao $Sn_{0.67}$-$Pd_{0.33}$ katalizator zbog boljeg iskorišćenja Pd. Primećeno je da kod $Sn_{0.67}$-$Pd_{0.33}$ katalizatora Sn bolje doprinosi oksidaciji hemisorbovanih čestica na Pd obezbeđivanjem OH čestica, omogućujući tako dobru sinergiju Sn sa Pd.
Ključne reči: *elektrohemijsko taloženje;elektrokatalizatori; elektrooksidacija; dendriti.*

Introduction

Direct alcohol fuel cells (DAFCs) have obtained considerable attention because of their promising commercialization as the power source for portable electronic devices and fuel-cell vehicles [1,2]. The use of alcohols as fuel has several advantages in regard to hydrogen, such as easy storage and transportation [3,4]. Ethanol is an attractive fuel because it has relatively high theoretical energy density, low toxicity and can be produced easily from the fermentation of maize, sugar came, wheat and some other raw materials [4]. With the development of anion-exchange membrane more attention has been paid to electrocatalysis in alkaline medium because the kinetics of alcohol oxidation enhanced as compared with that in acidic medium [3,5]. The design of active and poisoning tolerant anodic catalyst is major subject in the development of direct ethanol fuel cell (DEFC). Pd is a prospective substitute for Pt because of its relatively abundant reserves. Moreover, Pd presents high electrocatalytic activity for ethanol oxidation in alkaline medium [6]. Thus Pd-based catalyst is an excellent candidate for the application in DEFCs. Designing a new type of catalyst with less consumption of Pd metal by combining Pd with one or more transition metals such as, Sn [7,8], Cu

[9], Ag [10,11], Ni [12, 13], and adjusting their morphologies and compositions can further improve their electrocatalytic activity for ethanol oxidation.

We reported the synthesis of Sn sub-layer covered with a smaller fraction of Pd by means of two step electrodeposition technique [14]. According to morphological and elemental analysis of Sn and Sn–Pd, various forms of dendrites were obtained depending on the regime of Sn electrodeposition, while Pd on Sn creates electrodeposited islands [14-16]. It was demonstrated that the electrocatalytic activity of Pd in Sn–Pd depended strongly on the structure and morphology of dendrites [14]. Since Sn has no catalytic activity in the potential range of EOR [14], the electrooxidation of ethanol on the Sn–Pd catalysts is mainly attributed to the electrocatalysis of Pd component. The role of Sn is to contribute Pd to oxidize chemisorbed species formed during the electrooxidation of ethanol by providing adsorbed OH- species [17, 18], thereby enhancing the catalytic performance of the bimetallic catalysts. It was shown based on XPS measurements that the presence of Sn affects the electronic state of Pd by reducing the adsorption strength of the reaction intermediates on Pd, which has a positive effect on Sn-Pd electrocatalytic activity during the EOR [14]. By vary the amount of Sn loading prepared in the potentiostatic regime and keeping constant Pd loading, a series of Sn-Pd electrocatalysts with various ratios of Sn and Pd were synthesized and among them, $Sn_{0.6}$-$Pd_{0.4}$ showed to be the most active and poisoning tolerant catalyst in EOR [19].

In this work, the Sn-Pd electrocatalysts with various forms of Sn dendrites and different atomic ratios of Sn:Pd were prepared via a facile template-free two step electrodeposition technique. The electrocatalytic activity of Sn-Pd catalysts toward EOR were investigated by the electrochemical measurements.

Experimental

All the experiments were performed in three-compartment electrochemical glass cells with Pt electrode as the counter electrodes and Ag/AgCl/3.5 M KCl as the reference electrodes and all potentials were referred to this electrode denoted as Ag/AgCl. The electrolytes were prepared with high purity water (Millipore, 18M cm resistivity) and the chemicals provided by Merck. The experiments were conducted at 298±0.5 K. BioLogic SP 200 potentiostat/galvanostat was employed. Cylindrical electrodes of Cu, with a surface area of 0.25 cm^2 were used as substrate for Sn electrodeposition. Cu working electrode was prepared as described previously [15]. Sn electrodeposition was performed on Cu electrode from deaerated electrolyte containing 20 g/L $SnCl_2$ × $2H_2O$ in 250 g/L NaOH at a cathodic potential of −1.8 V or at a current density of −3 mA cm^{-2} [15]. After the Sn deposition, electrode was rinsed and transferred to the electrochemical cell containing deaerated 1 M NH_4Cl and 0.01 M $PdCl_2$. The electrodeposition of Pd was performed galvanostatically at a current density of −5 mA cm^{-2} [12]. Electrode obtained by electrodeposition of Sn at −3 mA cm^{-2} with the same amount of electricity like Pd (600 mC) was denoted as Sn(−3mA cm^{-2})-Pd while electrode prepared by electrodeposition of Sn at −1.8 V keeping the same condition for Pd electrodeposition was designated as Sn(−1.8 V)-Pd. Next set of electrodes were prepared with constant amount of electricity for Sn obtained by electrodeposition at −1.8 V (600 mC), while the amount of electricity for Pd varies (300, 900, and 1200 mC) to correspond the atomic ratio of Sn:Pd = 0.67:0.33 or 0.4:0.6 or 0.33:0.67. Depending on the atomic ratio electrodes were marked as $Sn_{0.67}$-$Pd_{0.33}$, $Sn_{0.4}$-$Pd_{0.6}$ and $Sn_{0.33}$-$Pd_{0.67}$. After preparation the electrode was rinsed with water and transferred into a cell containing 1 M NaOH with 1 M ethanol. EOR was examined using CV by scanning the potential starting from −0.8 to 0.2 V at a rate of 50 mV s^{-1}. In chronoamperometric measurements, the potential was stepped from −0.8 to −0.4 V. The reaction currents obtained in electrochemical experiments were normalized to the mass amount of Pd metal in catalysts.

Results and discussion

Influence of a regime of the electrodeposition

The electrochemical behavior of Sn-Pd catalysts was directed to examination of Sn deposition regime keeping the constant atomic ratio of 50 at.% Sn–50 at.% Pd. It was reported that the electrocatalytic activity of Pd in Sn-Pd depend strongly on the morphology of Sn [14]. Depending on the regime of Sn electrodeposition different morphology of the dendrites can be obtained [14, 15]. Thus for the Sn electrodeposition at constant current density ($j = -3$ mA cm^{-2}) two dimensional branchy dendrites with branches in a form of prisms were mainly created while when Sn was electrodeposited at constant potential ($E = -1.8$ V) the intertwined network of highly-branched fern-like dendrites was obtained. The selected current density for Sn deposition in galvanostatic regime is higher than the plateau of the limiting diffusion current density while the chosen electrodeposition potential is outside the plateau of the limiting diffusion current density[15, 16]. The synthetized electrocatalysts are denoted as Sn(-1.8V)-Pd and Sn(-3 mAcm^{-2})-Pd. Two well-defined peaks for ethanol oxidation are measured and presented in Fig. 1. The oxidation of newly chemisorbed species derived from the adsorption of ethanol can be detected by the peak in the forward scan while the reverse oxidation peak is mainly assigned to the removal of carbonaceous species that were incompletely oxidized in the forward scan [18]. According to Fig. 1 some lower activity of Sn(-3 mA cm^{-2})-Pd catalyst for Sn obtained at galvanostatic regime in regard to Sn(-1.8V)-Pd catalyst for Sn prepared at potentiostatic regime can be explained due to lower utilization of Pd on the Sn of certain morphology. It seems that intertwined network of highly-branched fern-like Sn dendrites provide better accessibility of Pd to EOR compared to dendrites with the branches of prismatic shape.
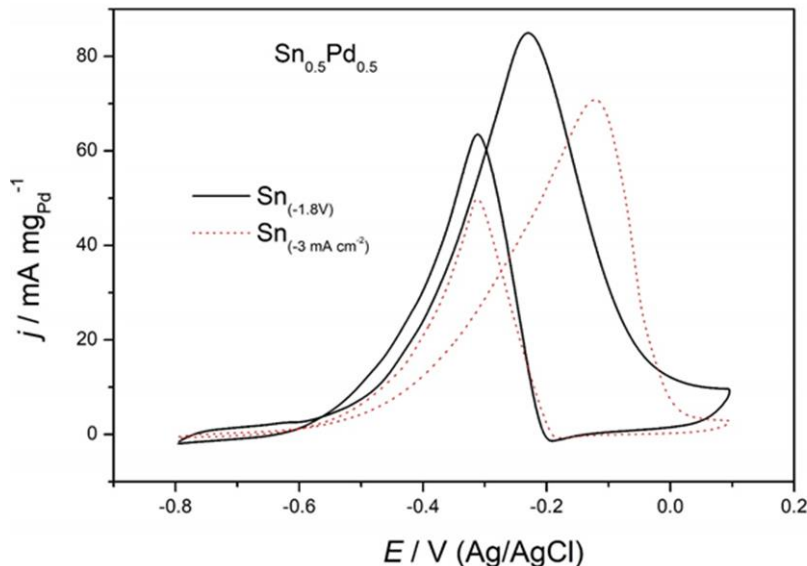
Figure 1.CVs of Sn$_{(-1.8V)}$-Pd and Sn$_{(-3\ mA\ cm}$$^{-2}$$_{)}$-Pd catalysts in 1 M NaOH +1 M C$_5$H$_5$OH solution recorded at v = 50 mV s^{-1}.

According to Fig. 1 Sn(-1.8V)-Pd catalyst has more negative initial potential (E_{in}) and more negative peak potential (E_p) value for approximately 0.1 V in regard to Sn(-3 mA cm^{-2})-Pd, indicating higher oxidation efficiency for EOR. It seems that Sn(-1.8V)-Pd catalyst more easily formed adsorbed OH$^-$ species due to appropriate Sn morphology and improve the ability to remove adsorbed intermediate species on Pd thus increasing the activity of the electrocatalyst.

The activity and the stability of Sn(−1.8V)-Pd and Sn(−3 mA cm^{-2})-Pd catalysts were also investigated by chronoamperometry. The current densities of EOR at a potential of − 0.4 V were traced over 20 min. The current-time transients presented in Fig. 2 show that the initial activity of Sn(−1.8V)-Pd catalyst is much higher compared with Sn(−3 mA cm^{-2})-Pd. The decrease of initial activity of 3.8 times for Sn(−1.8V)-Pd catalyst and 5 times for Sn(−3 mA cm^{-2})-Pd was observed over 20 min at a constant potential. Better stability of Sn-Pd catalyst for Sn prepared at potentiostatic regime in regard of Sn-Pd catalyst for Sn obtained at galvanostatic regime was established and that is in accordance with the results presented in Fig 1.
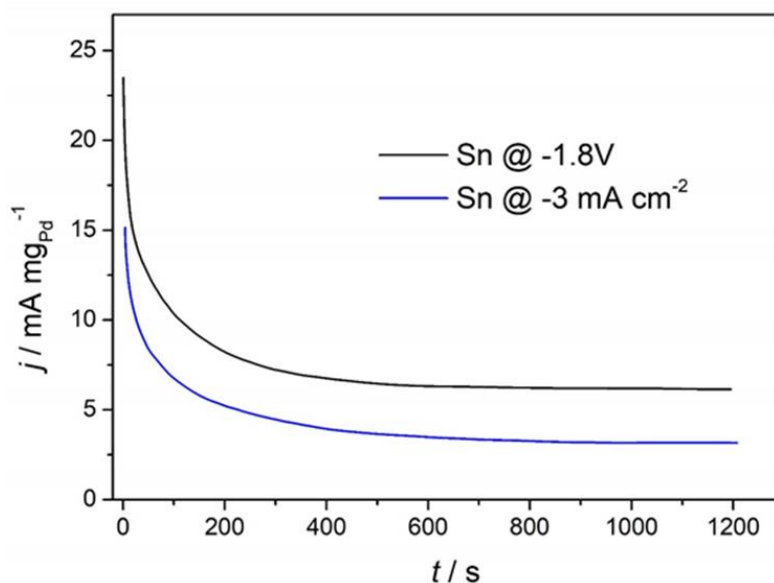

Figure 2. *Chronoamperograms of Sn$_{(-1.8V)}$-Pd and Sn$_{(-3\ mA\ cm}$$^{-2}$$_{)}$-Pd catalysts in 1 M NaOH +1 M C$_2$H$_5$OH solution recorded at E = −0.4 V.*

Effect of Pd deposited charge for constant current

Sn synthetized at −1.8 V creates networking of the dendrites and serve as substrate for deposition of Pd of various deposition charges under the same electrodeposition regime (−5 mA cm^{-2}). Namely it was necessary to ensure not only the loading of the Pd as the main catalyst, but sufficient reactive sites for the surface reaction of the catalysts and because of that fraction of Pd was vary. Figure 3 presents CVs recorded on Sn-Pd catalysts prepared for constant Sn deposited charge followed by Pd deposition at the constant current for various charges. According to Fig. 3 the most active one was found to be Sn$_{0.67}$-Pd$_{0.33}$, with the current densities of the forward peak being almost 2 times higher in regard to Sn$_{0.4}$-Pd$_{0.6}$ and Sn$_{0.33}$-Pd$_{0.67}$. In addition if the fraction of Pd in the Sn-Pd is too high, the catalytic performance of Pd will be obstructed, causing the decrease of the overall activity of Sn-Pd catalysts. Therefore better utilization of Pd with sufficient reactive sites for EOR was accomplished at Sn$_{0.67}$-Pd$_{0.33}$ catalyst. It seems that at Sn$_{0.67}$-Pd$_{0.33}$ catalyst Sn better contribute Pd to oxidize chemisorbed species coming from electrooxidation of ethanol by providing adsorbed OH$^-$ species, thereby facilitating well synergy of Sn with Pd. Besides lower E$_{in}$ and E$_p$ was achieved on Sn$_{0.67}$-Pd$_{0.33}$ electrocatalyst pointing out that this catalyst is more prone for use in the EOR compared to other Sn-Pd presented in Fig. 3.
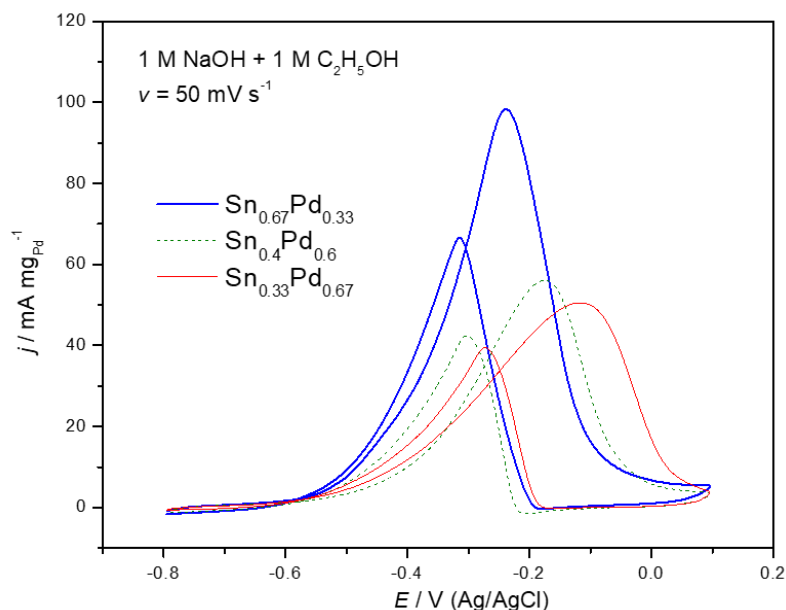
Figure 3.*CVs of Sn$_{0.33}$-Pd$_{0.67}$, Sn$_{0.4}$-Pd$_{0.6}$, and Sn$_{0.67}$-Pd$_{0.33}$ catalysts in 1 M NaOH +1 M C$_2$H$_5$OH solution recorded at v = 50 mV s^{-1}.*

Generally, the activity of electrocatalyst for EOR can be depicted by measuring the magnitude of the peak current density in the forward scan, while the ratio of the forward anodic peak current density (j_f) to the reverse anodic peak current density (j_b) is utilized to describe the tolerance of electrocatalyst to the accumulated intermediate carbonaceous species on the surface of electrode [20]. Thus a greater ratio of j_f/j_b implies higher completeness of ethanol oxidation during the forward scan as well as less carbonaceous residues accumulated on electrode surface. The obtained values of j_f/j_b are 1.10; 1.30; and 1.50 for Sn$_{0.33}$-Pd$_{0.67}$, Sn$_{0.4}$-Pd$_{0.6}$, and Sn$_{0.67}$-Pd$_{0.33}$, respectively, as illustrated in Fig. 4. Therefore Sn0.67-Pd0.33 exhibited the highest anti-poisoning ability.
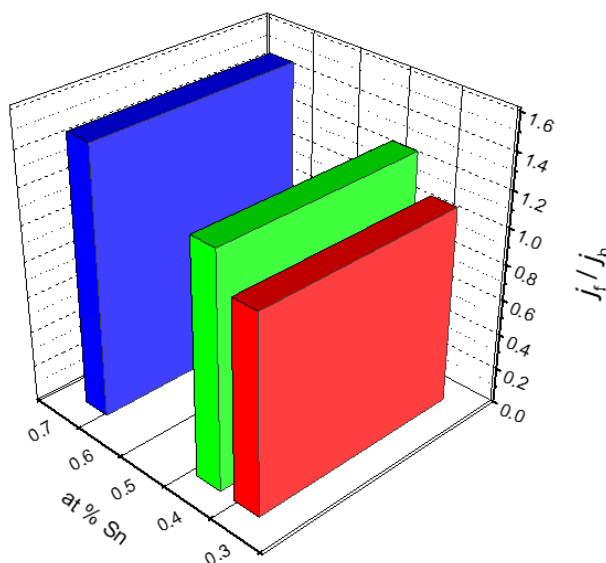

Figure 4.*Dependencies of j$_f$/j$_b$ from the fraction of Sn in Sn-Pd catalysts (data derived from Fig. 3).*

Conclusion

In summary, we reported the activity of Sn-Pd electrocatalysts in ethanol oxidation reaction. Impact of deposition conditions on electrochemical performances was presented. It was demonstrated that different morphology of Sn contribute and determine Pd electrochemical behavior in EOR thus the higher activity was obtained on Sn-Pd catalyst that contain Pd on intertwined network of highly-branched fern-like Sn dendrites as sub-layer in comparison to Pd on the Sn dendrites with the branches of prismatic shape. The highest activity and anti-poisoning ability exhibited $Sn_{0.67}$-$Pd_{0.33}$ catalyst due to the better utilization of Pd. At $Sn_{0.67}$-$Pd_{0.33}$ catalyst Sn better contribute Pd to oxidize chemisorbed species by providing adsorbed OH^- species, thereby enabling well synergy of Sn with Pd.

Acknowledgements

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