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Electrodeposited Pd-based alloy coatings as efficient catalysts for low temperature fuel cells application

Elektrohemijski taložene legure na bazi Pd kao efikasni katalizatori koji se primenjuju u niskotemperaturnim gorivim ćelijama

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Abstract

Electrodeposition of Pd–based coating samples of different thicknesses, depending on the coating composition and current efficiency, was achieved galvanostatically on the rotating Au disc electrode from the plating bath containing mixed solutions of their precursors. Determination of the alloy coating composition was performed by the anodic linear sweep voltammetry (ALSV) analysis and compared with spectroscopic measurements. Electrodeposited Pd and PdNi coating samples were tested for ethanol oxidation reaction (EOR) in alkaline solution. The current density and poisoning tolerance increased with increasing the amount of Pd in the PdNi coating. Examination of the EOR and oxygen reduction reaction (ORR) on electrodeposited Pd, Ag and AgPd alloy coatings of different compositions and morphologies demonstrated for the first time that the activity for the EOR and ORR at AgPd alloys was closely related to the amount of non-reduced Ag_2O (most probably as Ag-hydroxide).

Introduction

Among various types of fuel cells, the direct alcohol fuel cell (DAFC) has been considered as a promising energy source of portable and transportation application due to their low environmental impact, high theoretical energy density, and ease to accumulate and handle compared than other fuels [1]. For decades polymer electrolyte membrane fuel cells were investigated but almost exclusively in the acid medium. However, since the appearance of alkaline membranes, electrochemical investigations including ethanol and methanol oxidation reaction (MOR) as well as ORR, turned towards the alkaline medium [1, 2]. The alkaline media provides a less corrosive environment to the electrodes in regard to the acid medium. Moreover, one of the main advantages of alkaline medium comes from the fact that the electrode reaction kinetics in this medium is higher than in the acid medium, enabling the use of Pt-free catalysts. Recent studies have shown that Pd-based catalysts are very attractive for both alcohol oxidation reaction [2] and ORR [3] in alkaline medium, representing an important alternative to Pt-based catalysts for DAFCs. Numerous previously published results showed the noticeable catalytic properties of Pd but problems with durability signify the need of upgrading the Pd-based materials. In order to improve the performances of Pd catalysts, metals such as Au [4], Ag [5], Ni [6], Cu [7], or metal oxides [8] are usually added. Regarding the anode side reaction of DAFC, Pd-based catalysts have shown improved catalytic activity and poisoning-tolerant ability. Concerning the cathode side reaction, Pd-based catalysts have shown high ORR activity close to that of Pt.

In order to consider the catalytic activity, cost, stability, and long-term operation for electrocatalyst in industrial application, the development of new materials remains challenging. Synthesis of metal alloy nanoparticles by the electrochemical methods are extensively developed topic in materials science. Most of the synthesis methods use organic surfactants, capping agents or high temperatures, consequently heating or cleaning treatment are necessary and therefore, the catalytic activity can be affected by undesirable adsorbed species. Nevertheless, among the various methods, electrodeposition is recognized as a simple and versatile method to prepare bimetallic surfaces.

The aim of this work was to investigate the EOR on electrodeposited Pd, PdNi and AgPd alloy coatings of different compositions and morphologies. ORR was investigated on electrodeposited Ag, Pd and AgPd alloy coatings. The electrocatalytic performances were studied in order to correlate the composition, morphology and activity of coatings. Particular attention was given to the relevance and contribution of Ag-oxides in the EOR and ORR.

Results and discussion

ALSV analysis of electrodeposited coatings

The preparation of nanostructured materials by electrochemical procedures through simultaneous deposition of metals from the mixed solutions of their precursors has attracted considerable attention because these techniques allow variation of the crystallite size influencing on physical and chemical properties. Electrodeposition is an excellent technique for producing amorphous and nanocrystalline coatings.

Identification of phases in electrodeposited alloys for size of crystals lower than 10 nm by x-ray technique is often limited because they appeared as amorphous the on diffractograms and had to be identified by the other technique such as transmission electron microscopy (TEM). Nevertheless simple ALSV technique provide phase composition determination of different types of electrodeposited alloys [9]. The ALSV technique is based on the application of linear sweep voltammetry at low scan rate of 1 mV s^{-1} during the dissolution of a thin layer of electrodeposited alloy. Alloys were electrodeposited up to 10 μm thickness, from the solution containing ions of both metals in one cell. Immediately after the electrodepositing process, the electrode was transferred to another cell that contained electrolyte in which no passivation of any of the metals could take place, for complete dissolution.

It was possible to predict the shape of the ALSV of alloy dissolution by consideration of the phase diagram of alloys and the Gibbs energies of phases appearing in the system. Different types of alloys (eutectic [10], solid solution [9, 10], and alloys with intermediate phases and/or intermetallic compounds [10]) were investigated possessing different shapes of the ALSV responses. The PdNi as well AgPd systems belong to the solid solution-type alloys [10, 11] and taking into account standard potentials of pure metals, as well as the fact that the electrodeposition/dissolution of both metals is irreversible, two separate peaks for dissolution of each constituent of the alloy should be expected on the ALSV response. The PdNi [12] and AgPd [13] alloy compositions determined by the ALSV and EDS techniques are given in Table 1 and Table 2.

Table 1. Conditions of Pd and PdNi alloy coatings electrodeposition and their compositions determined by ALSV and EDS.

sample	j_d (mA cm^{-2})	Q_d (C cm^{-2})	ALSV		EDS	
			at % Pd	at % Ni	at % Pd	at % Ni
Pd	-9.1	-0.5	100	0	100	0
PdNi-1	−18.8	-0.5	80	20	74	26
PdNi-2	-60	-0.5	60	40	50	50
PdNi-3	-80	-0.5	40	60	28	72

Table 2. Conditions of Pd and AgPd alloy coatings electrodeposition and their compositions determined by ALSV and EDS.

sample	j_d (mA cm^{-2})	Q_d (C cm^{-2})	ALSV		EDS	
			at % Pd	at % Ag	at % Pd	at % Ag
Pd	-2	-1.0	100	0	100	0
AgPd1	-0.178	-0.2	24	76	16.2	83.3

AgPd2	-0.415	-0.2	8	92	9.8	90.2
AgPd2	-7	-0.3	13.4	86.6	3.4	96.6

EOR at electrodeposited Pd and PdNi alloy layers in alkaline solution

The EOR was investigated on the $Pd_{0.74}Ni_{0.26}$, $Pd_{0.50}Ni_{0.50}$, and $Pd_{0.28}Ni_{0.72}$ and Pd coatings by the CV. It was shown that the current density increased with the increase of Pd content up to 74 at. %. The most active one was found to be $Pd_{0.74}Ni_{0.26}$ with the lowest value of onset potential and highest poisoning tolerance among the studied coatings [12]. The contribution of Ni in the PdNi alloy concerning EOR in notable due to increasing the presence of OH species at the electrode surface. It was pointed out that improved catalytic activity of investigated binary coatings can be achieved through the optimization of the Ni content and appropriate surface morphology. The ability to recover activity loss demonstrates surface composition stability of investigated PdNi binary coatings [14].

EOR at electrodeposited Pd and AgPd alloy layers in alkaline solution

Three AgPd alloy samples were electrodeposited for the EOR investigation and compared with the sample of pure Pd, since pure Ag shows negligible catalytic activity towards the EOR [13]. It was shown that high catalytic activity for the EOR onto AgPd alloys can be obtained by cycling the electrodes to the potential of complete formation of Ag_2O indicating on the contribution of the amount of Ag-oxides. The percentage of non-reduced Ag_2O could be obtained according to the equation:

$$\%\ \text{non} - \text{reduced}\ Ag_2O = \frac{|\text{Qox}| - |\text{Qr}|}{|\text{Qox}|}\ 100(x_{Ag})$$

The absolute value of charge for Ag_2O reduction is $|Q_r|$; absolute value of charge for Ag_2O formation is $|Q_{ox}|$ the; the amount of Ag in the alloy is x_{Ag}. The dependence of the non-reduced Ag_2O for investigated coatings as a function of the atomic percentages of Pd is presented in Table 3.

Table 3. The dependence of the non-reduced Ag2O for investigated coatings as a function of the atomic percentages of Pd

Sample	$\%\ \text{non} - \text{reduced}\ Ag_2O$	at % Pd
Ag	1.3	0
AgPd1	12.9	27.4
AgPd2	6.05	13.4
AgPd3	14	15.2
Pd	0	100

The presence of non-reduced Ag_2O (Table 3), most probably in the form of AgOH, could act as oxygen source for the oxidation of carbonaceous species improving the EOR kinetics on Pd catalyst in alkaline solution through a bifunctional mechanism. The most active and the most poisoning tolerant are AgPd1 and AgPd3 alloy samples.

ORR at electrodeposited Ag, Pd and AgPd alloy layers in alkaline solution

The ORR on the Ag, Pd and AgPd alloys of different morphologie and compositions was investigated in alkaline solution saturated with oxygen. Significant catalytic activity for the Ag and AgPd alloys was detected after cycling electrodes in the potential region of Ag_2O formation and reduction [15]. Catalytic activity of AgPd alloys was found to be closely related to the amount of non-reduced Ag_2O, most probably in the form of Ag-hydroxide. This finding was support by XPS

measurements. The highest value of the kinetic current density was obtained for the alloy containing 27.4 at.% Pd (AgPd1).

Conclusion

Investigation of EOR on electrodeposited PdNi coatings showed that the magnitude of the currents increases as a function of palladium content. Better utilization of Pd on the surface of $Pd_{0.74}Ni_{0.26}$ coating is noticed due to appropriate surface morphology since more active sites are accessible to the EOR. Also improved catalytic activity of investigated binary coatings can be achieved through the optimization of the Ni content and appropriate surface morphology.
Alloying of Pd with Ag greatly reduces the amount of precious Pd metal in the catalyst, maintaining at the same time better catalytic activity for the EOR and ORR. Besides the investigated bimetallic coatings are less expensive electrocatalysts and this preliminary research indicates a possibility for practical application.

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