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S A D R Ž A J
C O N T E N T

The influence of Zn content on the activity of PtZn catalysts in methanol electrooxidation reaction

Uticaj sadržaja Zn na aktivnost PtZn katalizatora u reakciji elektrooksidacije metanola

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Abstract

This work highlights a simple and efficient approach for the development of PtZn catalyst materials with tunable content of Zn. Nanoparticles of PtZn deposited on high surface area carbon Vulcan XC-72R material were synthesized by microwave-assisted polyol method, giving control over the size and dispersion of nanoparticles. Cyclic voltammetry and electrooxidation of adsorbed CO were used to investigate the electrochemical behavior of synthesized catalysts: PtZn/C (90:10); PtZn/C (85:15) and PtZn/C (75:25). It was found that PtZn/C catalysts have high electrocatalytic performance in methanol oxidation reactions. In comparison to the corresponding catalyst with the different Zn loading, it was concluded that PtZn (90:10)/C catalyst had better activity compared to PtZn/C (85:15) and PtZn/C (75:25) catalysts. The observed high catalytic activity in the methanol oxidation reaction of synthesized catalysts can be ascribed to the very efficient microwave synthesis and well-balanced content of Zn as alloying metal.

Keywords: *Fuel Cell; Platinum Catalysts; Methanol electrooxidation*

Sažetak

Ovaj rad predstavlja jednostavan i efikasan pristup za razvoj PtZn katalizatora sa različitim sadržajem Zn. Nanočestice PtZn istaložene na ugljeničnom materijalu Vulcan XC-72R velike površine, sintetisane su poliol metodom

pomoću mikrotalasne pećnice, dajući kontrolu nad veličinom i disperzijom nanočestica. Za ispitivanje elektrohemijskog ponašanja sintetisanih katalizatora PtZn/C (90:10); PtZn/C (85:15) i PtZn/C (75:25) korišćeni su ciklična voltametrija i elektrooksidacija adsorbovanog CO. Utvrđeno je da PtZn/C katalizatori imaju visoke elektrokatalitičke performanse u reakcijama oksidacije metanola. Poređenjem katalizatora sa različitim sadržajem Zn, zaključeno je da PtZn/C (90:10) katalizator ima bolju aktivnost u odnosu na PtZn (85:15) i PtZn (75:25) katalizatore. Uočena visoka katalitička aktivnost sintetisanih katalizatora u reakciji oksidacije metanola može se pripisati veoma efikasnoj mikrotalasnoj sintezi i dobro izbalansiranom dodavanju Zn kao legirajućeg metala sa različitim sadržajem u PtZn/C katalizatorima.
***Ključne reči**: Gorivna ćelija; Platinski katalizatori; Elektrooksidacija metanola*

1. Introduction

The negative effects on the environment are consequences of industrialization and urbanization due to high energy consumption mainly obtained from non-renewable energy sources. Since non-renewable energy sources are in limited supply there is an increasing need for fuel cell technology development contributing to the potential reduction of fossil fuel use in the near future. Fuel cells like polymer electrolyte membrane fuel cells (PEMFCs) could produce electricity by using the chemical energy of hydrogen or small organic molecules such as methanol, ethanol or formic acid [1]. Despite their effectiveness, low operating temperature, high energy density and minimal impact on the environment, PEMFCs have several issues such as high production costs, as well as poor durability and reliability. Previous research has shown that the most active fuel cells are those containing platinum catalysts. Platinum (Pt) is one of the most expensive noble metals and a limited natural resource. Therefore, there is a need to reduce the amount of Pt in the catalysts whether to find more optimal and efficient ways of synthesis of the catalysts or alloying it with some less expensive metal such as Sn, Mo, Zn, Fe, Co, Au, Bi, Ni, etc. [2] [3] [4]. Due to its electronic structure, Zn could be interesting alloying metal. Since Zn has an empty 4(s,p) orbital and a fully filled 3d orbital and depending on the other metal alloying with it can be an electron donor or acceptor. The presence of Zn in the Pt/C influences the relocalization of electrons within Pt, i.e. the transition of electrons between orbitals (from its 5d to 6(s,p) orbitals) reducing the energy of the Pt 5d band in the PtZn alloy [5]. As a consequence, the adsorption bond strength of CO_{ads} which is the unwonted intermedier during the electrooxidation of fuels was weakened.

In this research, catalysts: PtZn/C (90:10); PtZn/C (85:15) and PtZn/C (75:25) were synthesized by microwave-assisted polyol procedure and further supported on carbon Vulcan XC-72R to obtain materials with better performances toward methanol electrooxidation. Three specific goals, achieved

by Zn loaded Pt, were: (1) reducing the Pt amount alloying with cheaper metal; (2) modification of the electronic characteristics of the Pt in purpose to reduce the adsorption strength of strongly adsorbed species such as CO; (3) creation of new catalysts for their practical applications in direct methanol fuel cell (DMFC).

2. Materials and Methods

2.1. Synthesis of catalysts

Nanoparticles of PtZn with different content of Zn were synthesized by the microwave-assisted polyol method. To obtain the PtZn/C catalysts, the same amount of 0.5 mL of 0.05 M H_2PtCl_6 solution and ethylene glycol (25 mL) was mixed with 0.15; 0.25 and 0.50 mL 0.05 M $ZnSO_4$ to obtain the PtZn (90:10); PtZn (85:15) and PtZn (75:25) catalysts, respectively. To adjust pH~12, 0.8 M NaOH was added dropwise. The prepared solutions were mixed for 30 min under magnetic stirring and then placed in the microwave oven for 90 s at 700 W for the reduction reaction. After microwave heating and colloids aging (48 h), the colloidal solutions were mixed with 20 mL of Vulcan XC-72R carbon water suspension and 150 mL 2 M H_2SO_4 for 3 h, prompting the homogeneous deposition of the colloids on the carbon support. The final suspensions were vacuum filtered, and the solid residues were rinsed with high-purity water (Millipore, 18 MΩ cm, Darmstadt, Germany). The solid products were dried for 3 h in an N_2 atmosphere at 160 ^oC. Metallic loading for all catalysts was adapted to 20 mass %.

2.2. Electrochemical Measurements

All electrochemical experiments have been performed at room temperature. The three compartments of an electrochemical cell were made: the saturated calomel electrode (SCE) was used as a reference electrode while Pt wire was used as the counter electrode. The electrocatalyst ink for the working electrode was obtained by ultrasonication of 2 mg of the synthesized catalyst in a suspension of 1 mL water and 50 μL of 5 % aqueous Nafion solution. The solution was ultrasonically treated for 1 h, and after that, 10 μL of the solution (catalyst loading of 20 g/cm^2) was placed onto the top of the working electrode (glassy carbon substrate) and dried for ~ 2 h at room temperature. The electrocatalytic activity of the prepared catalysts is studied in 0.5 M H_2SO_4 + 0.5 M CH_3OH solution using cyclic voltammetry. Methanol was added to the basic electrolyte solution at a constant electrode potential of −0.2 V.

The electrochemical surface area (ECSA) for each PtZn/C catalyst was calculated from adsorbed carbon monoxide (CO_{ads}) stripping voltammetry measurements. Carbon monoxide was introduced in the electrochemical cell

with 0.5 M H_2SO_4 for 15 minutes in order to obtain the saturated solution, followed by adsorption at the electrode surface while keeping the electrode potential at −0.2 V vs. SCE for 15 min. After adsorption, the electrodes were transferred into the cell containing N_2 saturated 0.5 M H_2SO_4 and the CO_{ads} was electrochemically oxidized at a sweep rate of 50 mV/s. All used chemicals were of analytical grade and supplied from Merck, while all solutions were made using high-purity water (Millipore, 18 MΩ cm, Darmstadt, Germany). Before each experiment, the electrolytes were saturated with N_2. For all electrochemical measurements AUTOLAB potentiostat/galvanostat PGStat 128 N (ECO Chemie, Utrecht, The Netherlands) was used.

3. Results and Discussion

3.1. Electrochemical Performance of the Catalysts

The cyclic voltammetry measurements were used to determine the electrochemical behavior of all PtZn/C catalysts. The basic cyclic voltammograms of all catalysts are illustrated in Figure 1.

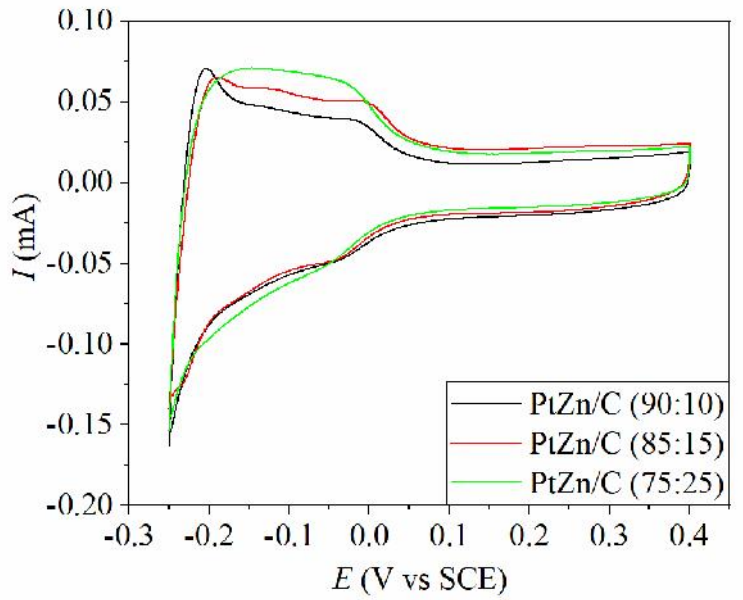

Figure 1. Cyclic voltammograms of PtZn/C (90:10); PtZn/C (85:15) and PtZn/C (75:25) catalysts in 0.5 M H_2SO_4, v = 50 mV/s.

The basic voltammograms of all synthesized PtZn/C catalysts presented at Figure 1 showed the well-developed hydrogen adsorption/desorption region. The obtained voltammograms of PtZn/C catalysts are in agreement with voltammograms reported in the literature for platinum catalysts synthesized in a similar procedure [6] [7].

3.2. Oxidation of adsorbed CO

Due to the tendency of CO_{ads} to be strongly adsorbed on active Pt sites, CO_{ads} is the unwanted product of the methanol electrooxidation reaction [8]. For that reason, the oxidation of CO_{ads} was carried out to establish a resistance to CO_{ads} poisoning of the examined catalysts and calculate ECSA.
Stripping curves for CO_{ads} of PtZn/C (90:10); PtZn/C (85:15) and PtZn/C (75:25) catalysts are presented in Figure 2. As can be seen from Figure 2, sharp peaks representing the oxidation of CO_{ads} and for all catalysts occurred at 0.60 V vs SCE. Investigating the oxidation of adsorbed CO (Figure 2), we noticed that the onset of the reaction starts by ~ 0.2 V for all catalysts.

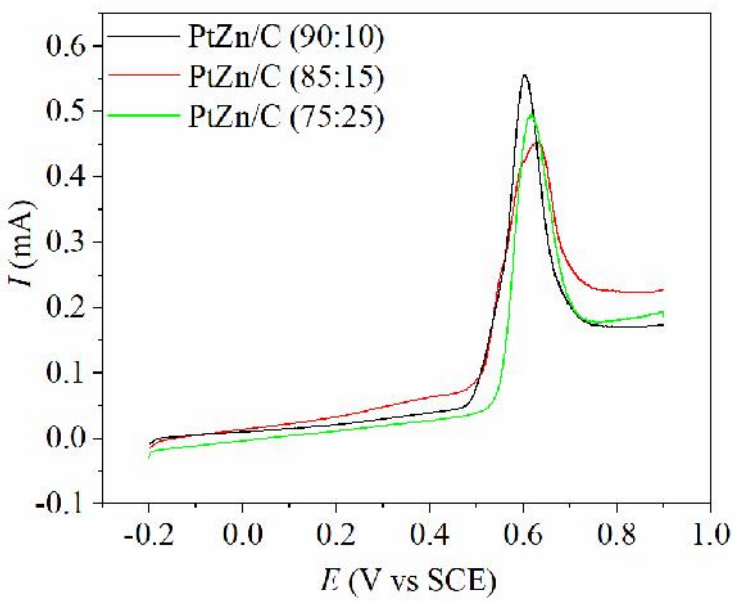

Figure 2. Oxidation voltammograms (stripping voltammograms) of adsorbed CO for as-prepared PtZn/C (90:10); PtZn/C (85:15) and PtZn/C (75:25) catalysts in 0.5 M H_2SO_4, v = 50 mV/s.

The ECSA values were calculated by integrating the stripping voltammograms in the potential region and summarized in Table 1. In order to normalize the activities of different electrocatalysts to the same number of Pt reactive surface sites, the determination of the real surface area is very important. The total charge transfer was determined by integrating the stripping voltammograms in the potential region, and the calculated electrochemically active surface areas (ECSAs) are summarized in Table 1. [8]. The ECSA values were calculated from CO stripping using a specific charge of 420 μC cm^{-2} regarding a monolayer of adsorbed CO [9]. As was expected PtZn/C (90:10) had the highest ECSA value compared to PtZn/C (85:15) and PtZn/C (75:25) (Table 1).

Table 1. The electrochemically active surface area (ECSA) of PtZn/C (90:10); PtZn/C (85:15) and PtZn/C (75:25) catalysts calculated from CO_{ads} stripping voltammetry

Catalyst	**PtZn/C (90:10)**	**PtZn/C (85:15)**	**PtZn/C (75:25)**
ECSA, cm^2	1.86	1.81	1.77

3.3. Methanol Oxidation

The activity of as-prepared PtZn/C catalysts for methanol oxidation was obtained from potentiodynamic measurements (Figure 3)

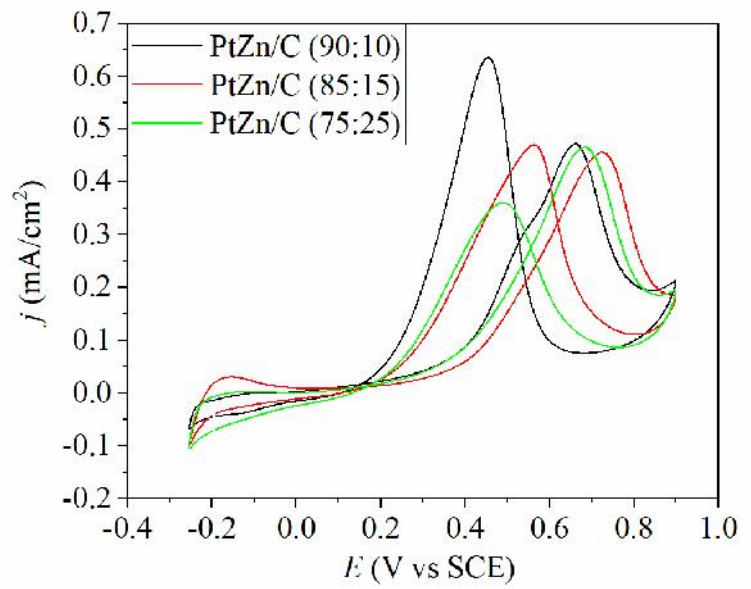

Figure 3. Cyclic voltammograms recorded in 0.5 M CH_3OH + 0.1 M $HClO_4$ at as prepared PtZn (90:10); PtZn (85:15) and PtZn (75:25) catalysts, v = 50 mV/s.

For the examined catalysts, as illustrated on Figure 3, the beginning of methanol electrooxidation is in the region where hydroxyl ion adsorption occurs (~ 0.1 V vs. SCE) [10]. It was noticed (Figure 3) that PtZn/C (90:10) catalyst compared to the PtZn/C (85:15) and PtZn/C (75:20) catalysts showed the best catalytic activity. It should be also emphasized that all PtZn/C catalysts poses better activity for methanol ectrooxidation reaction in comparison to the Pt/C catalyst synthesized by the same procedure [8]. The presence of Zn in all synthesized PtZn/C catalysts induces the formation of hydroxyl adsorbed species (OH_{ads}) (which are necessary for removing CO_{ads} species) during methanol oxidation at much lower potentials than in Pt/C catalysts and therefore promotes the elimination of CO_{ads}. Such influence of alloyed Zn is in literature well known as a bifunctional effect. Besides the bifunctional effect, the presence of alloyed Zn in PtZn/C catalysts causes the electronic effect. In the electronic effect, alloyed Zn reduces affinity for CO adsorption on such

catalysts, since Zn changes the electronic structure of platinum as a result of electron exchange between these two metals [8].

4. Conclusions

The focus of this research was the synthesis of PtZn/C catalysts with enhanced efficiency for the methanol oxidation reaction. In this work carbon-supported PtZn catalysts with different amounts of Zn were successfully synthesized by the microwave-assisted polyol procedure. Effective methanol oxidation, high electrocatalytic activity and good tolerance to poisoning species are also demonstrated. Comparing synthesized catalysts, it can be concluded that the PtZn/C (90:10) shows better activity compared to the other two materials. Well-designed bimetallic structure of the examined catalysts, for the purpose of use in DMFC, provides the possibility of reducing the amount of expensive noble metal (Pt) with a less expensive metal such as Zn.

Acknowledgments

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