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S A D R Ž A J
C O N T E N T

Mikrotalasna sinteza platinskih legura za uspesnu oksidaciju metanola u gorivnim spregovima

Microwave-assisted synthesis of Pt-alloy catalysts for successful methanol oxidation reaction in fuel cells

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Izvod

Ova studija je fokusirana na pronalaženje novih načina sinteze katalizatora na bazi platine koji pokazuju dobru efikasnost za reakciju oksidacije metanola. Nanočestice PtZn, PtSn i PtSnZn su sintetizovane korišćenjem poliol metode uz pomoć mikrotalasnog zagrevanja i deponovane na ugljeničnu podlogu Vulcan XC-72R. Elektrohemijsko ponašanje sintetizovanih katalizatora je ispitivano korišćenjem ciklične voltametrije i hronoamperometrijske tehnike. Fizičkohemijska svojstva dobijenih katalizatora su okarakterisana transmisionom elektronskom mikroskopijom (TEM), termogravimetrijskom analizom (TGA) i energetsko disperzivnom spektroskopijom (EDS). Prema TEM analizi svi katalizatori imaju male čestice prilično slične veličine između 1 i 3 nm. Dobijeni rezultati su potvrdili uspešnu sintezu katalizatora na bazi Pt. Dodavanje Zn i Sn u Pt katalizator značajno poboljšava aktivnost oksidacije metanola u poređenju sa Pt/C referentnim katalizatorom. Testovi stabilnosti takođe dokazuju slabije trovanje i ukazuju na bolju stabilnost i veću toleranciju na CO intermedijere. Uočena visoka katalitička aktivnost i dobra stabilnost u reakciji oksidacije metanola sintetizovanih katalizatora mogu se pripisati veoma efikasnoj mikrotalasnoj sintezi i dobro izbalansiranom sadržaju Zn i Sn kao legirajućih metala.

***Ključne reči**: Platinski katalizatori; Elektooksidacija metanola; Mikrotalasna sinteza;*

Abstract

This study is focused on novel ways for creating Pt alloy catalysts that are more effective for the methanol oxidation reaction. PtZn, PtSn and PtSnZn nanoparticles were produced using the microwave assisted polyol method and were supported on high surface area carbon Vulcan XC-72R material. The electrochemical behaviour of synthesized catalysts was investigated utilizing the cyclic voltammetry and chronoamperometric technique. To determine the

catalyst's physicochemical characteristics, transmission electron microscopy analysis (TEM), energy dispersive spectroscopy (EDS) and thermogravimetric analysis (TGA) were used. According to TEM analysis all catalysts have small particles of rather similar size between 1 and 3 nm. The obtained results confirmed the successful synthesis of Pt-based catalyst. Addition of Zn and Sn to Pt significantly improves methanol oxidation activity in comparison to Pt/C benchmark catalyst. Stability tests also prove the lower poisoning and indicate better stability and higher tolerance to CO-like intermediaries. The observed high catalytic activity and good stability in the methanol oxidation reaction of synthesized catalyst can be ascribed to the very efficient microwave synthesis and well-balanced content of Zn and Sn as alloying metal.

Keywords: *Platinum Catalysts; Methanol Electooxidation; Microwave Synthesis;*

Introduction

Fuel cells with methanol (DMFC) as fuel are very promising sources of energy for stationary and portable electrical devices primarily due to their high efficiency and low emissions of pollutants, low operating temperature, high energy density, non-toxic and environmentally friendly characteristics. However, their wider commercial use is limited by factors such as: the high cost of the precious metal in the electrocatalyst (for example, Pt) and poor operational durability, i.e. rapid degradation of the catalyst. Also, pure Pt catalysts are easily poisoned by strongly adsorbed species such as CO_{ads} intermediate produced by methanol oxidation during the electrocatalytic reaction. In order to reduce the cost of catalysts and improve their performance, many strategies have been initiated, most of them based on the synthesis of platinum catalysts in which platinum is alloyed with cheaper metals such as Ru[1], Sn[2], Ni[3], Zn [4] etc.. These metals can improve catalyst activity by facilitating the oxidation of highly adsorbed species blocking the platinum surfaces formed during the oxidation reaction of highly adsorbed carbon intermediates at much lower potentials compared to platinum. In this work PtZn/C, PtSn/C and PtSnZn/C catalysts were synthesized by microwave-assisted polyol method and their electrochemical activity and stability was tested for methanol electrooxidation reaction.

Experimental

Catalyst preparation

PtZn, PtSn and PtSnZn nanoparticles were synthetized by microwave assisted polyol method. To obtain these catalysts, 0.5 ml of 0.05 M H_2PtCl_6 solution and 25 ml of ethylene glycol were mixed with 0.5 ml 0.05 M $ZnSO_4$ solution for

PtZn/C catalyst and 0.5 ml 0.05 M $SnCl_2$ for PtSn/C catalyst. In order to obtain the PtSnZn/C catalyst, the same amount of platinum and ethylene glycol were mixed with 0.25 ml 0.05 M $ZnSO_4$ and 0.25 ml 0.05 M $SnCl_2$ solutions. The reduction reaction was carried out by microwave irradiation at 700 W for 90 s. After microwave heating, the colloidal solution was mixed with 20 ml of Vulcan XC-72R carbon water suspension and 150 ml 2 M H_2SO_4 for 3 h. The final suspension was filtered by vacuum pump and the solid residue was rinsed with high purity water. The solid product was dried for 3h in an N_2 atmosphere at 160 ^{0}C. The metal loading for all catalysts was adjusted to 20 mass %.

Physicochemical characterisations

PtZn/C, PtSn/C and PtSnZn/C catalysts were investigated by the thermogravimetric (TGA) and differential thermal (DTA) analyses performed in the range of 30-1000 ^{0}C range on a SDT Q600 TGA/DSC instrument (TA Instruments). The chemical composition of all catalysts were obtained by a scanning electron microscope (SEM) Tescan VEGA TS 5130 MM supplied with energy-dispersive X-ray spectroscopy (EDS) detector INCAPentaFET-x3, Oxford Instruments. Transmission electron microscope (TEM) JEM-1400 with an accelerating voltage of 120 kV was employed for detailed characterization of the morphology of the produced catalyst.

Electrochemical characterisations

The electrocatalytic activities of catalysts were examined in 0.5 M H_2SO_4 + 0.5 M CH_3OH solution. Catalysts stabilities were examined by long-term potential cycling and chronoamperometric method. The specific catalyst activities are normalized in relation to the values of platinum mass loading. AUTOLAB potentiostat / galvanostat PGStat 128N (E CO Chemie, The Netherlands) was employed for electro-chemical measurements.

Results and discussion

PtZn/C, PtSn/C and PtSnZn/C catalysts were analysed by the TGA/DTA analysis, and EDX examination. The results for TGA and EDX were presented in Table 1.

Table 1. TGA and EDS analyses for PtZn/C, ptSn/C and PtSnZn/C catalysts.

Catalyst	Metal content from TGA (mass %)	The Pt:Zn atomic ratios	
		Nominal (mass %)	EDS (mass %)
PtZn/C	27.68	75 : 25	87 : 13
PtSn/C	19	50 : 50	54 :46
PtSnZn/C	22.87	63 : 21 : 12	70 : 21 : 9

TGA analysis determined for the PtZn/C and PtSnZn/C catalysts slightly higher value of residual mass in comparison to the nominal value and it can be attributed to the presence of ZnO in the catalyst which can increase the reaction extent during the heating procedure.
According to the TEM study, the particle sizes of all catalysts were fairly similar, the observed catalyst particles have diameters of 1.63±0.3 nm for PtZn/C catalyst, 2.5±0.8 nm for PtSn/C catalyst and 1.8±0.4 nm for PtSnZn/C catalyst.

Methanol oxidation
The activities of the *as prepared* PtZn/C, PtSn/C and PtSnZn/C catalysts for methanol oxidation reaction were evaluated from potentiodynamic measurements (Fig. 1).

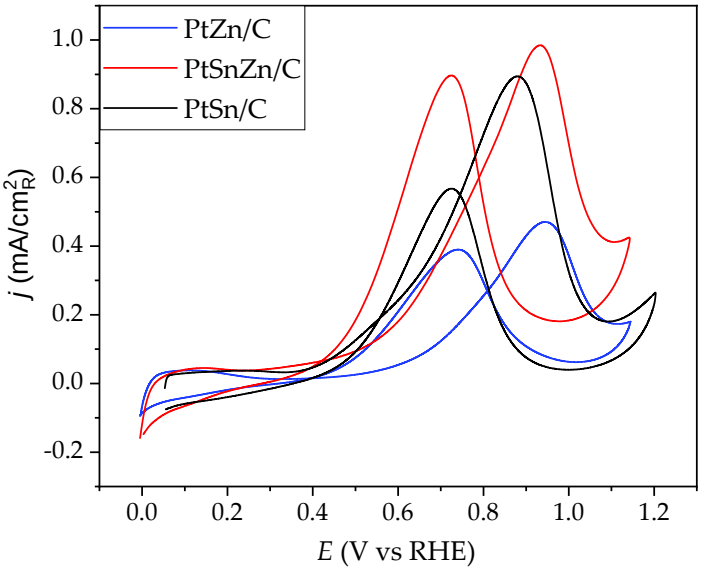

Fig. 1. Potentiodynamic measurements of the as prepared PtZn/C, PtSn/C and PtSnZn/C catalysts for 0.5 M CH_3OH electrooxidation reaction.

Based on the electrochemical tests related to the PtZn/C, PtSn/C and PtSnZn/C catalysts, the best performance showed the PtSnZn/C catalyst. The maximum forward activities of all catalysts are presented in Table 2.

Table 2. Summary of maximum forward activity for synthesised PtZn/C, PtSn/C and PtSnZn/C catalysts.

Catalyst	J_{max}(mA/cm^2$_R$)
PtZn/C	0.47
PtSn/C	0.88
PtSnZn/C	0.99

Analyzing the CVs from Fig.1 it can be noticed that for methanol oxidation reaction for all catalysts, peak current in forward (anodic) scan is higher than in reverse (cathodic) scan. Since the peak in reverse scan is due to removal of intermediates formed during the forward scan than the ratio between peak currents in the forward and backward scan (j_f/j_b) can be used to define the catalyst tolerance to carbonaceous species [5]. As a matter of fact, a higher ratio corresponds to a lower j_b peak, which suggests that less unwonted CO molecules adsorbed on the catalyst surfaces. This ratio is highest for PtSn/C catalysts for methanol electrooxidation reaction and suggests higher resistance versus poisoning intermediate products. Compared with commercial Pt/C E-TEK catalysts and Pt-Sn-Zn catalysts reported in the literature, our PtSnZn/C catalysts showed greater activity for the methanol electrooxidation reaction [6-9]. All values for j_f/j_b ratio are summarized in Table 3.

Table 3. Summary values of j_f/j_b of PtZn/C, PtSn/C and PtSnZn/C catalysts for methanol electooxidation reaction.

Catalyst	J_f/J_b
PtZn/C	1.2
PtSn/C	1.56
PtSnZn/C	1.14

Conclusions

The microwave assisted poliol method was used to sucsessfull syntesis of carbon supported Pt-Sn-Zn catalysts with enhanced efficiency for the methanol electrooxidation reaction. The results from cyclic voltammetry experiments related to methanol oxidation reaction showed that the best catalytic activity and improved resistance ability to CO inhibition is achieved after addition of Zn and Sn to Pt catalyst. Pt-Sn-Zn/C catalysts offer the opportunity to decrease the amount of pricey noble metals in DMFC since they have superior MOR activity than commercial Pt catalysts and catalysts reported in the literature.

Acknowledgments

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