CDKZM
CRNOGORSKO DRUŠTVO ZA KOROZIJU, ZAŠTITU MATERIJALA I ZAŠTITU ŽIVOTNE SREDINE

INŽENJERSKA KOMORA CRNE GORE
ENGINEERS CHAMBER OF MONTENEGRO

ČETVRTI MEĐUNARODNI SIMPOZIJUM O KOROZIJI I ZAŠTITI MATERIJALA, ŽIVOTNOJ SREDINI I ZAŠTITI OD POŽARA

FOURTH INTERNATIONAL SYMPOSIUM ON CORROSION AND MATERIALS PROTECTION, ENVIRONMENTAL PROTECTION AND PROTECTION AGAINST FIRE

KNJIGA RADOVA
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PdNi legure kao efikasni katalizatori u oksidaciji aklohola

PdNi alloys as efficient catalysts for alcohol oxidation

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Izvod

Ispitivane PdNi legure su dobijene elektrohemijskim taloženjem iz rastvora koji sadrži oba metala (0.01M $PdCl_2$ + 0.6M$NiCl_2$ + 2 MNH_4Cl). Elektrodeponovani PdNi uzorci su testirani za reakciju oksidacije metanola (MOR) i etanola (EOR) u alkalnoj sredini metodom ciklične voltametrije i hronoamperometrije. Pokazano je da se reakcione struje za MOR i EOR na PdNi legurama povečavaju sa sadržajem paladijuma u leguri. Uporedno ispitivanje elektrohemijske oksidacije alkohola u alkalnom rastvoru ustanovljava da među ispitivanim legurama $Pd_{0.74}Ni_{0.26}$ *ima najveću katalitičku aktivnost, dobru toleranciju prema akumulaciji ugljeničnih čestica i dobru postojanost.*

Abstract

The investigated PdNi alloys were prepared by electrochemical procedures through simultaneous deposition of metals from the mixed solutions of their precursors (0.01M $PdCl_2$ + 0.6M$NiCl_2$ + 2 MNH_4Cl). Electrodeposited PdNi samples were tested for methanol and ethanol oxidation reaction (MOR and EOR) in alkaline solution using cyclic voltammetry (CV) and chronoamperometric (CA) measurements. Investigation of MOR and EOR on electrodeposited PdNi alloys show that the magnitude of the currents increases as a function of palladium content. Comparative study of alcohol electro-oxidation in the alkaline solution reveals that $Pd_{0.74}Ni_{0.26}$ alloy has a higher catalytic activity, better tolerance to accumulation of carbonaceous species among the studied electrodes and good durability.

Introduction

Electrochemical deposition of metals on different substrates plays an important role in many modern technologies. While the search for less expensive electrodes for Alkaline direct alcohol fuel cells (ADAFCs) application has been a topic of interest, very few attempts have been made to examine electrodeposited alloys as electrodes for possible application in methanol or ethanol fuel cells. Anode catalysts with high catalytic activities as well as good poison resistances are of great significance to the commercialization of

ADAFCs. For alcohol oxidation in alkaline media, Pd-based nanocatalysts are superior to Pt-based catalysts and are widely used as anode catalysts in ADAFCs [1,2]. Developing Pd- and Ni-based electrocatalysts with high catalytic performances as substitutes for Pt catalysts contributes to theoretical and practical relevance to encourage the commercialization of ADAFCs.
The goal of this work is to investigate the electrochemical behavior of electrodeposited PdNi alloys for the alcohol oxidation in 1 M NaOH from the point of activity, stability and durability.

Experimental

All experiments were carried out with an VoltaLab PGZ 402 (Radiometer Analytical, Lyon, France) at room temperature in three compartment electrochemical glass cells with Pt wire as the counter electrode and saturated calomel electrode (SCE) as the reference electrode. Electrodeposition of PdNi alloys was achieved galvanostatically on the rotating Au disc electrode from the plating bath composed of 0.01 M $PdCl_2$ + 0.6 M $NiCl_2$ + 2 M NH_4Cl. All the conditions are the same as it was described in previous work [3].Behavior of electrodeposited PdNi alloys during the alcohol oxidation was recorded in the solution containing 1 M (CH_3OH or C_2H_5OH) + 1 M NaOH by using CV at 1000 rpm. For CA responses of alcohol oxidation the potential was stepped from -800 mV to -400 mV.

Results and discussion

The alcohol oxidation on PdNi alloys was investigated by CV. The dependences of forward currents (j_f) on the atomic percentage of Pd in electrodeposited PdNi alloys, taken at E = –300 mV for alcohol oxidation are shown in Fig. 1. The reaction current for MOR and EOR increases with enhancement of palladium content in electrodeposited PdNi coatings and the most active is found to be $Pd_{0.74}Ni_{0.26}$ [**Error! Bookmark not defined.**,4]. It seems that the small amount of Ni is sufficient to improve the electrocatalytic activity by increasing the presence of OH species at the electrode surface necessary of the oxidation of intermediates [5].

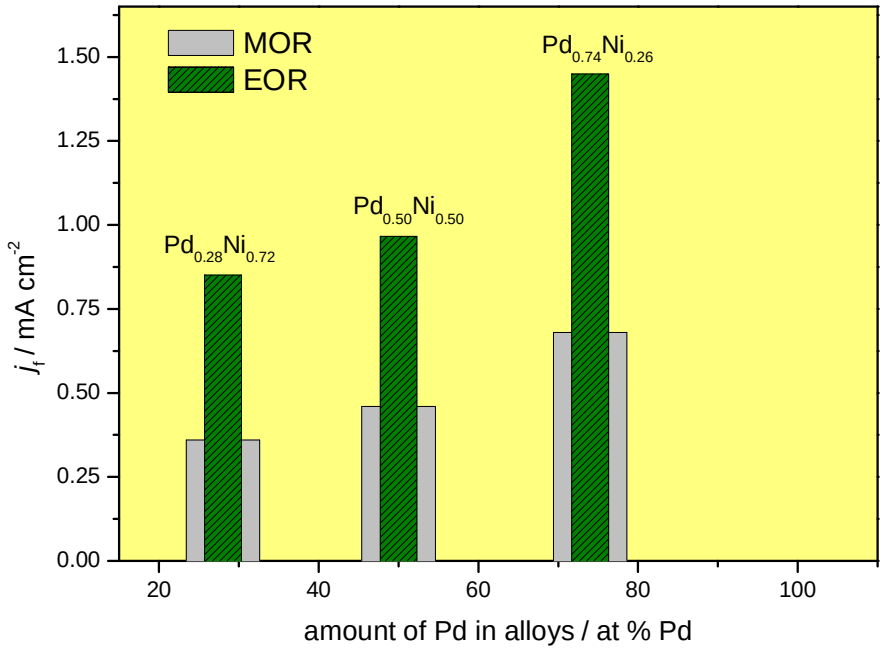

Fig. 1 Dependence of the j_f taken at E = –300 mV for MOR and EOR on the atomic percentage of Pd in the PdNi alloys.

The electrochemical stability of $Pd_{0.74}Ni_{0.26}$ alloy as the most active among the studied samples in alcohol oxidation was tested by chronoamperometric measurements at E = –400 mV as is presented in Fig. 3. The polarization current for alcohol oxidation shows a rapid decay due to the formation of intermediates and poisoning species, but after ~ 20 min, a pseudo-steady state is achieved.

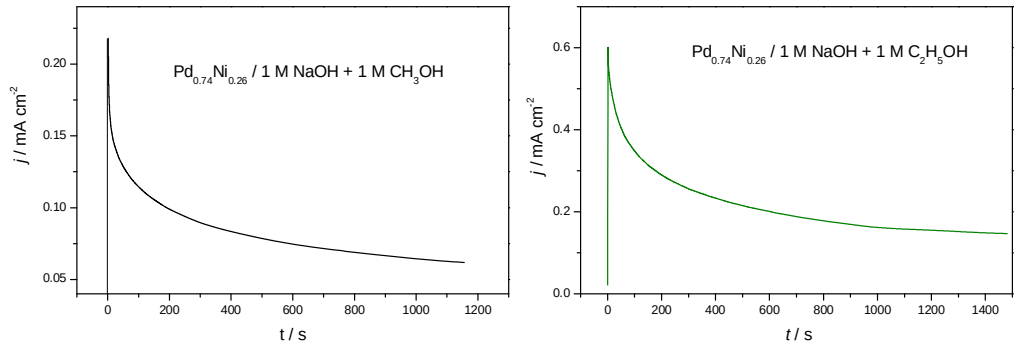

Fig.3. Current density–time responses recorded on $Pd_{0.74}Ni_{0.26}$ alloy in 1 M CH_3OH+ 1 M NaOH (a) and 1 M C_2H_5OH+ 1 M NaOH (b) at E = – 400 mV. RPM = 1000.

Durability of PdNi alloy was further investigated by scanning 100 cycles in alkaline electrolyte solution and the corresponding change of peak current density was shown in Fig. 4. At first the peak current densities decrease as the number of cycles increases from 1 to 30 for MOR and up to 20 for EOR. After that, the peak current densities of $Pd_{0.74}Ni_{0.26}$ remained almost constant indicating the good stability and almost negligible surface poisoning by reaction intermediates. The peak current density remains about 82% of its initial value after 100 cycles for EOR and 78 % for MOR. These results demonstrate that selected $Pd_{0.74}Ni_{0.26}$ alloy catalyst possesses the improved catalytic activity and durability in alcohol oxidation.

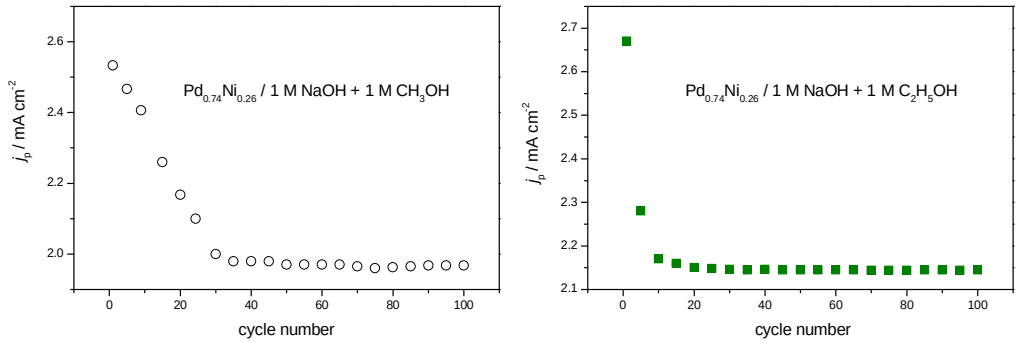

Fig. 4. The peak current density in the forward scan versus cycle number curves of $Pd_{0.74}Ni_{0.26}$ alloy in 1 M NaOH + 1 M CH_3OH (a) and 1 M C_2H_5OH+ 1 M NaOH (b).

Conclusions

Comparative study of methanol and ethanol electro-oxidation in the alkaline solution reveals that $Pd_{0.74}Ni_{0.26}$ alloy has a higher catalytic activity, as well as a better tolerance to accumulation of carbonaceous species among the studied electrodes. Durability of PdNi alloy was investigated by continuously cycling and the peak current density remains about 82% of its initial value after 100 cycles for EOR and 78 % for MOR. The obtained findings confirms that electrodeposited PdNi coatings show several perspective characteristics in alcohol oxidation.

Acknowledgments

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