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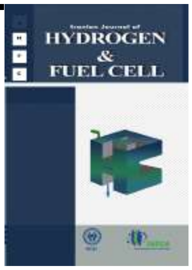

Electrochemical evaluation of electrodeposited platinum on a modified carbon substrate with cobalt, nickel and copper doped zinc oxide for the methanol oxidation reaction

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Abstract

Recently, methanol fuel cell systems have been attracting research activities by improving electrocatalysts to investigate facilitating the methanol oxidation reaction. ZnO and ZnO doped with other metals or metal oxide can be used as an additive in the carbon substrate of an electrocatalyst to improve electro catalytic properties of a platinum electrocatalyst. In this work, a simple low temperature hydrothermal method has been used for synthesis of different morphologies of 1% mol Ni, Cu and Co doped ZnO nanostructures. The prepared nanostructures were used in the carbon substrate of a platinum electrocatalyst on carbon paper. Then platinum was electrodeposited by simple cyclic voltammetry on a modified carbon substrate of the electrocatalyst. Prepared electrodes were investigated for methanol oxidation reaction in a three electrode half-cell system by electrochemical methods like as linear sweep voltammetry. The results revealed that with using Ni doped ZnO in carbon substrate, the current density was increased. While, with using Cu doped ZnO in carbon substrate, a significant reduction in anodic over voltage was observed.

1. Introduction

Direct Methanol fuel cells have attracted great scientific interest for potential application in electronic vehicles and portable devices due to their low operating temperature, low pollution emissions, high power density and easy handling [1–3]. The most efficient catalysts for both anode

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and cathode are by far platinum and platinum-based materials [4-5]. However, the high cost of these electrocatalysts and the limited natural abundance of platinum hinders its commercialization in large-scale applications. Therefore, there exists a considerable interest in developing new effective electrocatalysts (enhancing electro catalytic activity and durability and reducing the cost) [6–7]. Different materials have been studied as possible electrocatalysts: Pt-based nanomaterials with non-precious metals or metallic oxides (Ni, Fe, Co, CoO, etc.), Pt nanostructures with high porosity or different shapes, and non-precious metals or their oxides [8-13].

Among different electrocatalysts, metal or metal oxide nanostructures in carbon substrate is considereda good candidate for fuel cell application. Compared with pure Pt, the addition of these materials may not only improve the performance of electrocatalysts but also decrease Pt usage [14-16]. So, finding new effective supports or substrates for Pt deposition is of considerable interest. Among different deposition methods, the electrodeposition technique has been found to be a more convenient and promising method that can be manipulated in order to produce a high surface area of Pt [17-19].

In this work, we synthesized different morphologies of ZnO nanostructures doped with 1% molar ratios of Ni, Cu and Co in a simple low temperature hydrothermal method. Then, these nanostructured materials were used in carbon substrate and Pt was electrodepositied on them. These electrocatalysts were then used in the electrochemical study of the methanol oxidation reaction.

2. Experimental

2.1. Synthesis of electrocatalysts

2.1.1.Preparation of Co, Cu or Ni doped zinc oxide nanostructures

All of the chemical reagents used in the experiments were analytic grade without further purification and treatment. All products were prepared using a simple hydrothermal method at low temperature. We used $CoCl_2$, $CuCl_2$ or $NiCl_2$ as dopands. The molar ratio of these dopands with respect to Zinc acetate was 0.01. First, 3 mmol $Zn(CH_3COO)_2.2H_2O$ was dissolved in 50 ml distilled water at room temperature under stirring. Then, we added 3 mmol (1.2 g) sucrose ($C_{12}H_{22}O_{11}$) into this solution with vigorous stirring for 30 min. Next, we added 0.03 mmol of Co, Cu or Ni chloride to the above solution under stirring for 30 min. After that, 6 mmol NaOH powder (molar ratio of NaOH to Zinc acetate 2:1) was added under stirring and the solution was then transferred to an autoclave and kept at 100^0C in the oven for 2 h. After completion of the reaction time, we filtered the products via centrifugation and washed it with double distilled water several times until free from impurities such as chloride. Finally, the obtained products were dried at room temperature and then collected for physical characterization.

2.1.2. Preparing the modified carbon paper with doped ZnO

The sonication method (power of 40 w) was used in distilled water, nitric acid and acetone in a 1:1:1 mixture for 10 minutes to prepare modified carbon paper (12 mm diameter). Then the modified carbon paper was dried at 80 °C for 30 minutes in the oven. A paste composition (according Table.1) was used preparing prepare a modified carbon paper with carbon substrate and additives. The materials were completely mixed in a solvent of isopropanol using the sonication method (power of 40) for 20 minutes. The prepared paste was placed on a carbon paper and dried at 80°C for 30 minutes.

2.1.3. Platinum electrodeposition on the modified carbon paper

A solution containing 1 mM $H_2PtC_{16}.6H_2O$ and H_3PO_4 was used Platinum The cyclic voltammetry (CV) method (potential range: -0.25 V to 0.65 V vs. Ag/AgCl, scan rate 50 mV s^{-1}, room temperature) was applied to a three-electrode electrochemical cell to deposit platinum nanoparticles on modified carbon paper.

2.2.Electrochemical test

The electrochemical study of the methanol oxidation reaction (MOR) was made in a three electrode half-cell system at 1.0 M KOH and 1M methanol. A CV test was conducted from -1 to 1 V vs. Ag/AgCl at 100 mVs^{-1} scan rate. The linear sweep voltammetry (LSV) method was conducted from -1.25 to 0.5 V vs. Ag/AgCl at 1 mVs^{-1} scan rate.

3. Results and Discussion

Fig. 1 shows the scanning electron microscopy (SEM) images of the samples. As shown in this figure, Cu doped ZnO and Ni doped ZnO are structured as rods with hexagonal plate cross sections. The Co doped ZnO is formed of shorter rods with hexagonal plate cross sections. As shown in this figure, the crystallite sizes of Ni doped ZnO are smaller than the other structures.

The performance of the prepared electrocatalysts for methanol oxidation reaction was investigated using the CV (-1 to 1 V vs. Ag/AgCl) and LSV methods (-1.25 to 0.5 vs. Ag/AgCl) in 1.0 M KOH and 1 M methanol at room temperature.

Fig. 2 shows the CV curves of the prepared electrodes for the methanol oxidation reaction in alkali media. Cyclic voltammetry data shows the presence of methanol oxidation reduction related peaks in the prepared electrodes. These peaks display the location and peak intensity of the methanol oxidation reaction changed by varying the doping element in the ZnO substrate as compared to the pure state

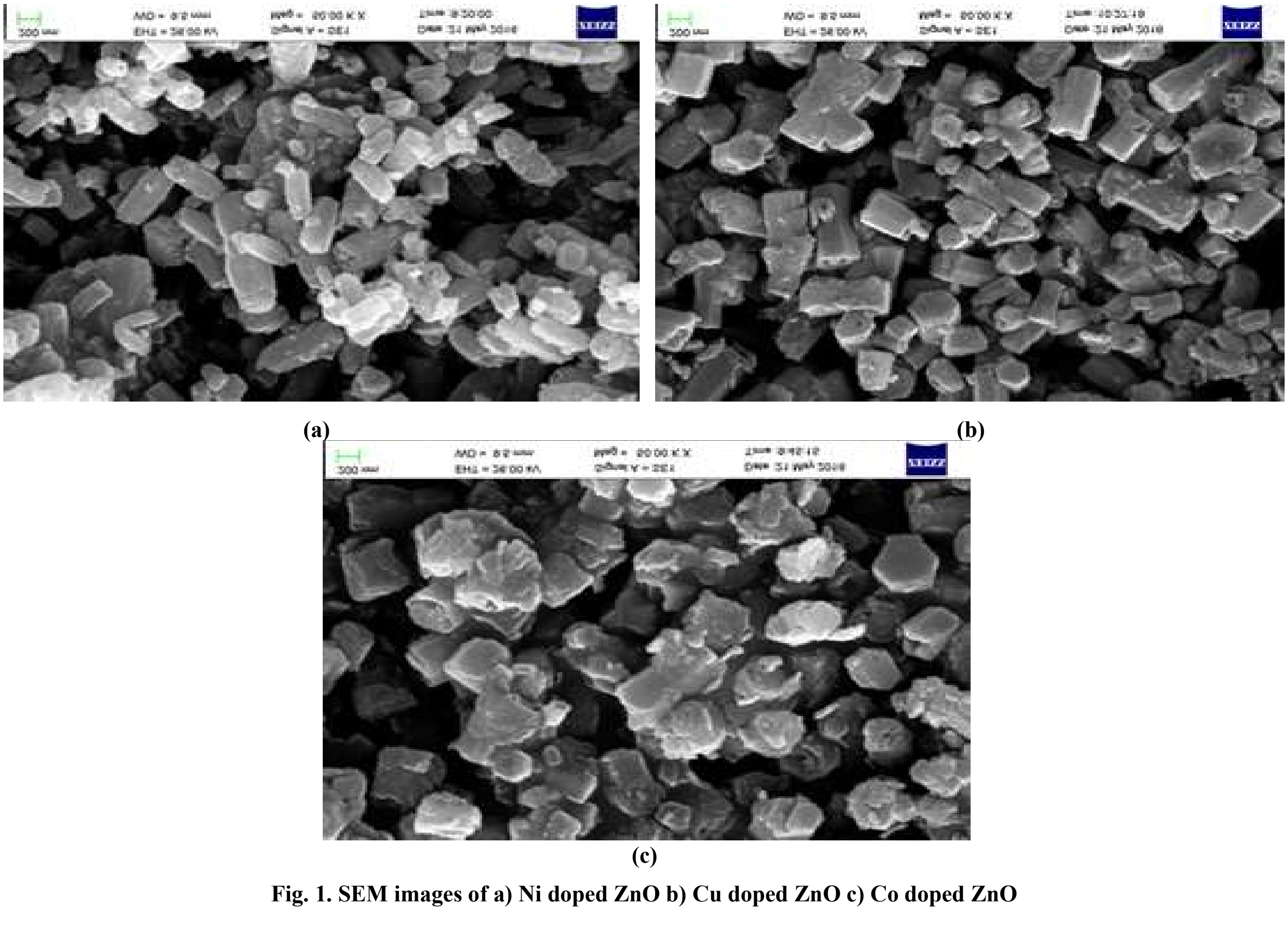

Fig. 1. SEM images of a) Ni doped ZnO b) Cu doped ZnO c) Co doped ZnO

Table 1.The paste composition of the electrode substrate

electrode	The paste composition of the electrode substrate				The amount of Vulcan / $mgcm^{-2}$	The amount of Ni,Cu and Co doped ZnO /$mgcm^{-2}$	PTFE / $mgcm^{-2}$
	Ni doped ZnO	Cu doped ZnO	Co doped ZnO	Vulcan			
A (Ni doped ZnO)	0.9	0.1	2.1	*	-	-	*
B (Cu doped ZnO)	0.9	0.1	2.1	*	-	*	-
C (Co doped ZnO)	0.9	0.1	2.1	*	*	-	-

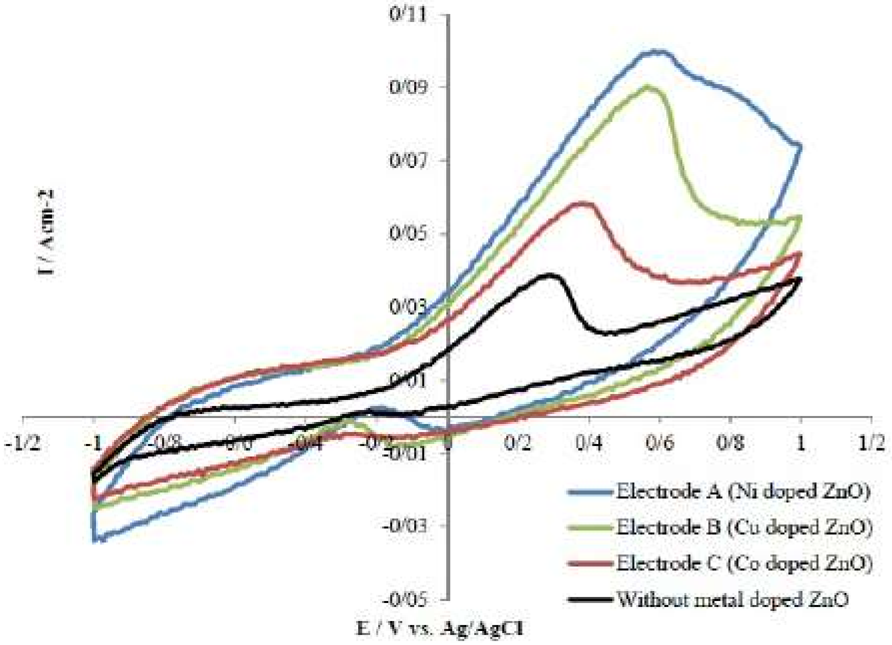

Fig. 2. Cyclic voltammogram of prepared electrodes with various substrate composition at the scan rate of 100 mV s^{-1} in 1.0 M KOH and 1 M methanol at room temperature

(without metal doped ZnO). This is very evident in the comparison of electrode A to C. However, the methanol oxidation reaction peak of the platinum electrocatalyst containing Ni or Cu doped ZnO is not significantly different. According to these results, the maximum current density of the methanol oxidation reaction was observed in electrode A, and is related to the presence of Ni doped ZnO in the reaction layer of the electrode.

Table 2 shows the electrochemical data of the prepared electro catalysts according to the LSV results (Fig. 3). LSV data shows the open circuit voltage (OCV) of the synthesized electrocatalyst is different with various dopands in the carbon substrate. So that, the presence of Cu in the carbon substrate of the electrocatalyst results in the more negative open-circuit potential for the methanol redox reaction. The obtained exchange current density (i_0) from the Tafel equation shows a high rate of methanol oxidation reaction in the platinum electrocatalyst containing Cu doped ZnO compared with other dopands in the carbon substrate of a Pt electrocatalyst. According to our results, despite the fact that the presence of Cu doped ZnO intends to increase the kinetics for the methanol oxidation reaction, the optimum performance of the prepared electrodes at a high current density area is related to the presence of Ni doped ZnO in the carbon substrate of the modified electrode. Therefore, the methanol oxidation reaction can occur with high mass transfer rate at this electrode. An interesting point in the performance of platinum electrocatalysts containing dopands is that despite the high kinetic polarization of Pt electrocatalyst containing Ni doped ZnO at the

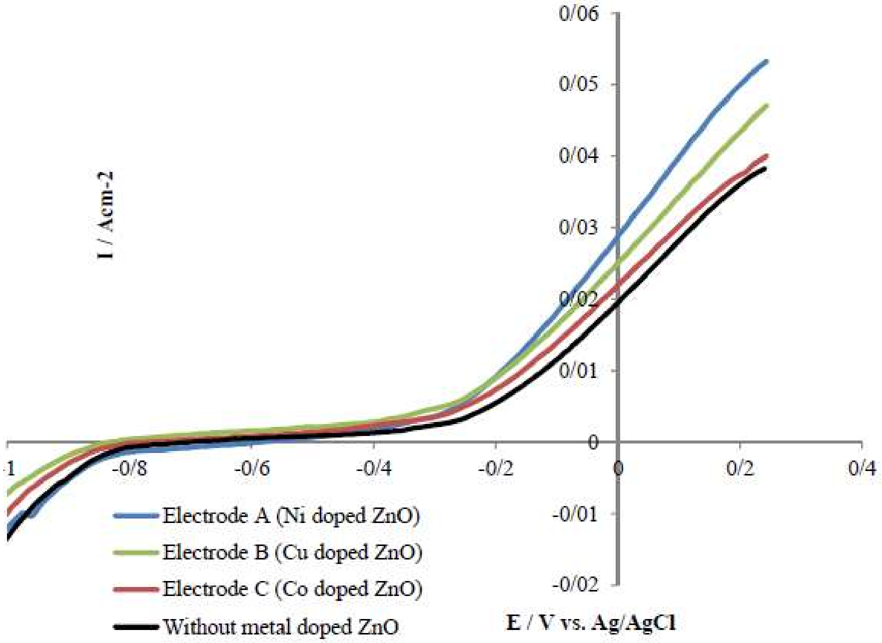

Fig. 3. LSV curves of fabricated electrodes with various substrate composition at the scan rate of 1 mV s^{-1} in 1.0 M KOH and 1 M methanol at room temperature

Table 2.The electrochemical properties of fabricated electrodes at various substrate composition

Electrode	OCV vs. Ag/AgCl / V	Current density at various voltages vs. Ag/AgCl			mAcm^{-2}
		-0.3 V / mAcm^{-2}	0.0 V / mAcm^{-2}	0.2 V / mAcm^{-2}	
Electrode A (Ni doped ZnO)	-0.575	3.48	28.8	50	0.37
Electrode B (Cu doped ZnO)	-0.828	4.60	25.1	43.4	0.82
Electrode C (Co doped ZnO)	-0.767	3.39	21.9	37.4	0.36
Without metal doped ZnO	-0.701	2.35	19.6	36.3	0.29

open circuit voltage with respect to electrode B (Cu doped ZnO), the methanol oxidation reaction at the surface of this electrocatalyst is faster than the other electrodes at the concentration polarization area.

However, the different electronic structures of these dopands may be responsible for this behavior during the interaction with a platinum electrocatalyst. In addition, SEM images of Ni doped ZnO structures show smaller crystallite structures than other samples, this may have an effect on the electrochemical properties of the platinum electrocatalyst.

4. Conclusion

In the present work, new electrocatalyst substrates based on Ni, Co, and Cu doped zinc oxide are introduced for the electrodeposition of platinum. These substrates could be good candidates in the preparation of electrodes for the methanol oxidation reaction. The presence of Ni, Cu and Co doped ZnO in the platinum electrocatalyst has an effect on the performance of electrodes for the methanol oxidation reaction. Our study shows that the electronic structures of dopands used in the reaction layer of the prepared electrodes effects the electron transfer kinetics and mass transfer of reactants of the methanol oxidation reaction. Therefore, the electro catalyst substrate electronic structure influences the performance of the electrodeposited platinum on the surface of this substrate used for the methanol oxidation reaction.

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