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The use of a hierarchically platinum-free electrode composed of tin oxide decorated polypyrrole on nanoporous copper in catalysis of methanol electrooxidation

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ABSTRACT

Tin oxide nanoparticles were synthesized through a galvanostatic pathway on polypyrrole, PPy, coated nanoporous copper. The morphology and surface analysis of the assemblies were evaluated by field emission scanning electron microscopy, FESEM, and energy dispersive X-ray, EDX, analysis, respectively. The electrocatalytic behavior of electrodes was studied by cyclic voltammetry and chronoamperometry tests in methanol solution. FESEM results showed that uniformly distributed nanoparticles with diameters of about 20–30 nm have been dispersed on PPy matrix. Cyclic voltammetry and chronoamperometry tests in methanol solution showed a significant enhancement in the catalytic action of PPy after decoration of tin oxide nanoparticles. Porous Cu/PPy/SnO_x electrodes showed enhanced anodic peak current density for methanol oxidation compared to smooth Cu/PPy/SnO_x and porous Cu/PPy. The effects of synthesis current density and time on the electrocatalytic behavior of the electrodes were evaluated. The significant enhancement of electrocatalytic behavior of the Cu/PPy electrode after decoration of SnO_x overlayer was attributed to the effect of tin oxide on the adsorption of intermediates of methanol oxidation as well as oxidation of bi-products such as CO; huge tendency of tin oxides for dehydrogenation of the alcohols and the increase in microscopic surface area of the electrodes were introduced as other affecting factors.

1. Introduction

Methanol electrooxidation is the main electrochemical reaction in a direct methanol fuel cell, DMFC. Methanol is a liquid fuel that is easy to store and transport. It also has high energy content and can be used in every pH values from acidic to alkaline solutions. The DMFCs directly transform the chemical energy of methanol into electricity, through the electro-catalytic reactions. During this process, the methanol is oxidized to carbon dioxide and other products; carbon monoxide is also produced as a bi-product of this reaction. The transformation of methanol to carbon dioxide is kinetically slow; so, a suitable catalyst is required to enhance the efficiency of this oxidation process [1]. Electrochemical oxidation of methanol on pure platinum and platinum-based catalysts has been widely evaluated. However the high cost of platinum and the strong adsorption of CO molecules on its surface are the main difficulties with platinum-based catalysts. The reactions that are responsible for production of poisoning agents have been reported as follows [2]:

$$Pt + CH_3OH_{sol} \rightarrow Pt-(CH_3OH)_{ads} \quad (1)$$

$$Pt-(CH_3OH)_{ads} \rightarrow Pt-(\bullet CH_2OH)_{ads} + H^+ + e \quad (2)$$

$$Pt-(CH_3OH)_{ads} \rightarrow Pt-(CH_3O^-)_{ads} + H^+ + e \quad (2')$$

$$Pt-(\bullet CH_2OH)_{ads} \rightarrow Pt-(\bullet CHOH)_{ads} + H^+ + e \quad (3)$$

or

$$Pt-(CH_3O^-)_{ads} \rightarrow Pt-(CH_2O^-)_{ads} + H^+ + e \quad (3')$$

$$Pt-(\bullet CHOH)_{ads} \rightarrow Pt-(\bullet CHO)_{ads} + H^+ + e \quad (4)$$

or

$$Pt-(\bullet CH_2O^-)_{ads} \rightarrow Pt-(\bullet CHO)_{ads} + H^+ + e. \quad (4')$$

During steps 1–4′, the formyl like species, $(\bullet CHO)_{ads}$, are formed and then decompose to $(\bullet CO)_{ads}$ on pure platinum according to step 5:

$$Pt-(\bullet CHO)_{ads} \rightarrow Pt-(\bullet CO)_{ads} + H^+ + e. \quad (5)$$

Finally the CO species are formed and strongly adsorbed on platinum surface; it leads to the poisoning of the catalyst.

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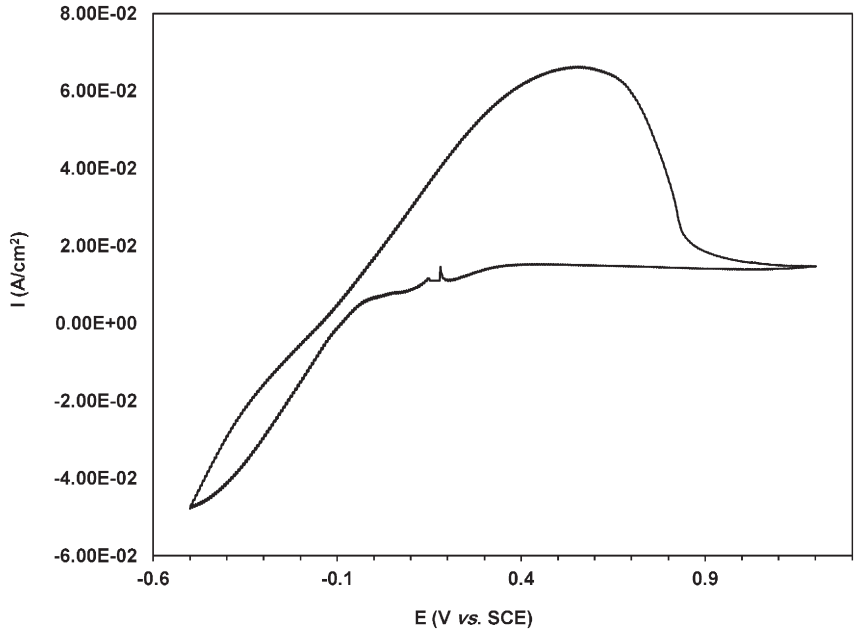

Fig. 1. Cyclic voltammogram of a Cu electrode in 1.0 M KCl solution at room temperature, scan rate of 100 $mV \cdot s^{-1}$.

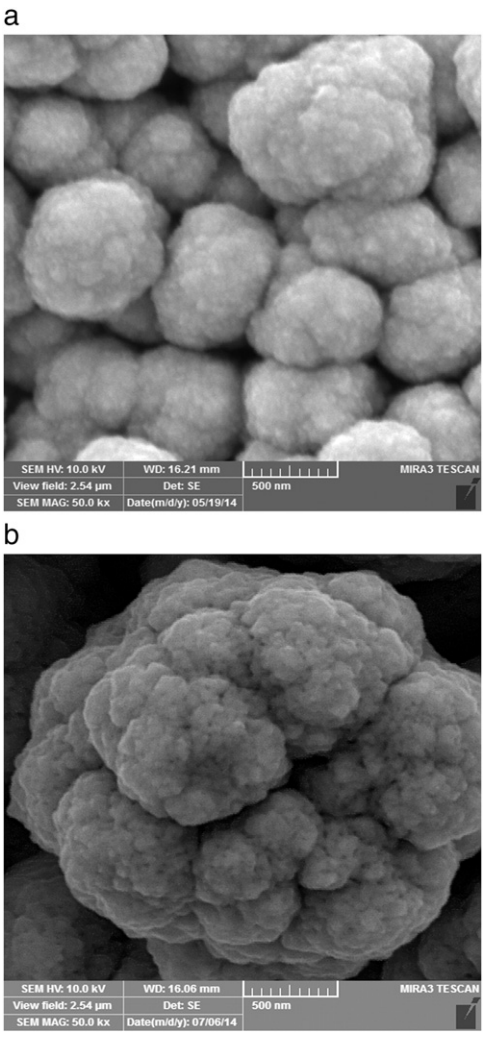

Fig. 2. FESEM images of electrodeposited Cu–Zn alloy (a) before and (b) after chemical leaching of zinc in acid solution (The nanopores are seen with diameters less than 10 nm).

The incorporation of foreign metals such as iridium and palladium, as alloying elements and/or as deposited overlayers, to the platinum matrix is one of the ways to consequence the poisoning problem [3]. Metals such as palladium, indium, tin, ruthenium, rhodium, titanium, *etc*. have been reported as alloying or composite materials for Pt-based electrodes [4,5,6,7]. Carbon supported metal nanoparticles are another candidates [8,9,10,11]. Several non-platinum catalysts for methanol oxidation have been investigated during the recent years [12,13,14,15,16,17]. Hosseini et al. have reported several works about the electrocatalytic activity of non-platinum electrodes such as Ni, Au and Ti on different matrices such as TiO_2 nanostructures and polyaniline nanofibres [1,8].

Tin and tin oxides have also been considered as an active material in the platinum-based as well as non-platinum catalysts for oxidation of alcohols in fuel cell applications [6,12,18,19,20]. Tin (IV) oxide, SnO_2, has also been investigated as a possible substitute for graphite as anode of Li-ion batteries [21,22]. Since the size of semiconducting metal oxide nanoparticles affects their properties, these materials can be used in a range of applications such as gas sensors, catalysts, photocatalysts, solar cells and so on [23]. Different methods have been developed to synthesize tin oxide nanoparticles such as high energy ball milling, homogeneous precipitation, sonochemical, hydrothermal, solvothermal, microemulsion and sol–gel routes, spray pyrolysis, polymerized complex citrate route and non-aqueous approaches [24]. However, most of these techniques require difficult and effortful synthesis conditions. The electrochemical synthesis routes, therefore, have become more desired due to their feasibility, rapidity and relatively low costs. By an electrochemical method, the synthesized material can be deposited directly on solid electrode with no need of additional procedures.

Table 1
EDX analysis results for the electrodeposited Cu–Zn alloy on copper electrode before and after leaching of zinc.

Conditions	Element	Wt.%
Before leaching	Cu	71
	Zn	25
	O	4.0
After leaching	Cu	85
	Zn	10
	O	5.0