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Full Length Research Paper

A novel Modified Electrodes as Methanol Fuel Cell Nano-Electrocatalysts

Mohamed Abdel Fattah Ibrahim[1],[2], Hossam Rageb[3]

[1]Chemistry Department, Faculty of Science, University of Tabuk71491, KSA
[2]Chemistry Department, Faculty of Education in El-Arish, Egypt
[3]Physics Department, Faculty of Education in El-Arish, Egypt
E-mail: science1712@gmail.com

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We prepared serial Pt/Ru/Carrier and Pt/Ni/Carrier electrocatalysts (Carrier = Alumina), which were deposited on the GC electrode. The prepared nanocomposites electrodes show about five times more for the electrocatalytic oxidation of methanol in sulphuric acid than Pt/Alumina/GC electrode.

Keywords: Electrocatalytic oxidation, Methanol, Pt nanoparticles

INTRODUCTION

Direct methanol fuel cell (DMFC) is considered as one of the most promising options for solving energy crisis in future, because of its high-energy conversion efficiency, low- pollutant emission, low operating temperature, and simplicity of handling and processing of liquid fuel (Lin et al., 2005; Huang et al., 2006; Prabhuram et al., 2007; Chen et al., 2006; Stevens and Dahn, 2003). Before the commercialization of DMFC, one of the critical problems is the poisoning of Pt electrocatalysts by carbon monoxide. This is because of strong adsorption of CO on the Pt surface, thus forming Pt–CO species, which inhibits the hydrogen oxidation reaction (Liu et al., 2004), (Li et al., 2007). To resolve this, bimetallic metals containing Pt are widely used to regenerate the inactive Pt–CO sites. It is generally recognized that PtRu alloys are currently the most active electrocatalysts for reducing the poisoning of CO (Li et al., 2006), (Yao et al., 2006). Watanabe et al. have proposed the bifunctional mechanism in which Ru acts as a promoting center for the generation of Ru–OH species (Huang et al., 2006), (Li et al., 2007):

$$\mathbf{Ru + H_2O \rightarrow Ru\text{-}OH + H^+ + e^-} \qquad \mathbf{(1)}$$

The adsorbed Ru–OH would effectively oxidize the poisoning CO into CO_2 through the following reaction:

$$\mathbf{Pt\text{-}CO + Ru\text{-}OH \rightarrow Pt + Ru + CO_2 + H^+ + e^-} \qquad \mathbf{(2)}$$

Thus, more Pt surface sites become available for methanol oxidation. However, though the presence of Ru facilitates the removal of CO adsorbed on Pt, thus releasing the occupied active sites, the effectiveness of reactions (1) and (2) still depends on the atomic ratio of PtRu alloy. Another important factor in determining the electrochemical activity of PtRu is the increasing surface area of the alloy catalysts. To attain higher activity, the commercial anode catalysts for DMFCs, namely carbon black, are well embedded with PtRu/Carrier and PtNi/Carrier particles. However, recent studies progressively focused on the PtRu alloy impregnated on another form of carbon material, namely carbon

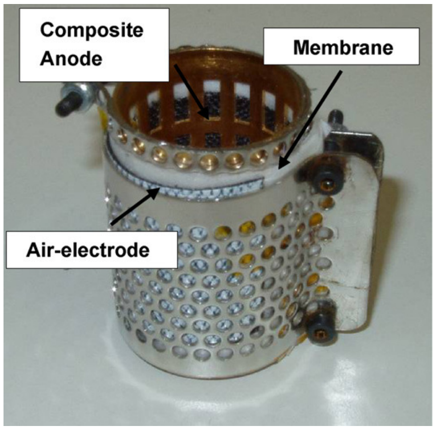

Figure 1. Tubular fuel cell design

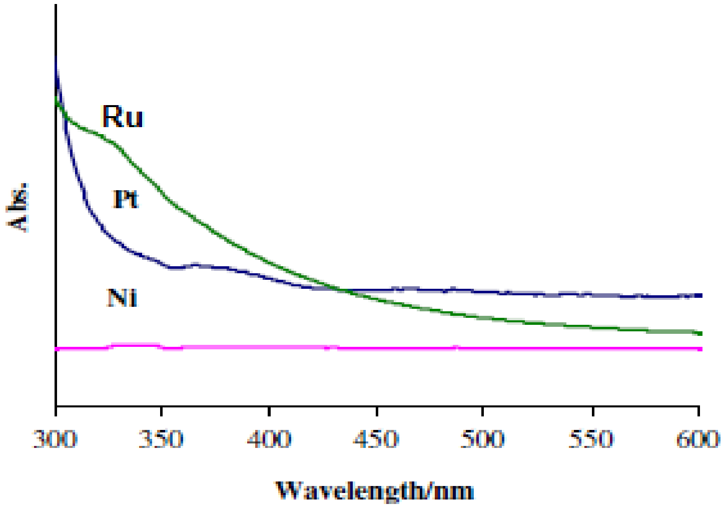

Figure 2. Absorption spectra of metal-Alumina nanocomposite

nanotubes (CNTs), which exhibited higher electrochemical activities (Xing, 2004 ; Che et al., 1999; Kongkanand et al., 2006; Jeng et al., 2007 ; Chien and Jeng, 2006 ; Wang et al., 2004). This indicates that CNTs play an important role in enhancing the electrochemical activity of the catalysts, even though the underlying mechanism is not clear. Additionally, although significant advances have been achieved in the electrochemical characterization of PtM/Alumina and PtM/Alumina anodes, the optimal atomic ratio of bimetallic PtRu and PtNi alloy that affect the electrochemical activity for methanol oxidation is not well understood.

In this work, we prepare serial Pt/Ru/Carrier and Pt/Ni/Carrier electrocatalysts (Carrier = Alumina), which were deposited on the GC electrode. These bimetallic alloys were found to possess a high degree of crystalline state with uniform particle size (ca. 3–4 nm). This study made an attempt to explore the electrochemical characterization of PtRu/Carrier/GC and PtNi/Carrier/GC catalysts and their catalytic activities in the electrooxidation of methanol.

Experimental

MATERIALS AND METHODS

We used the following materials H_2PtCl_6, $NiCl_2$, $Ru(NO_3)_2$, $MgCO_3$ and $NaBH_4$ obtained from Sigma-Aldrich. All solutions were prepared using doubly distilled water. Before each voltammetric experiment, nitrogen bubbling was used to deoxygenate the electrolyte solutions for 20 minutes. All the experiments have been done under nitrogen atmosphere at room temperature.

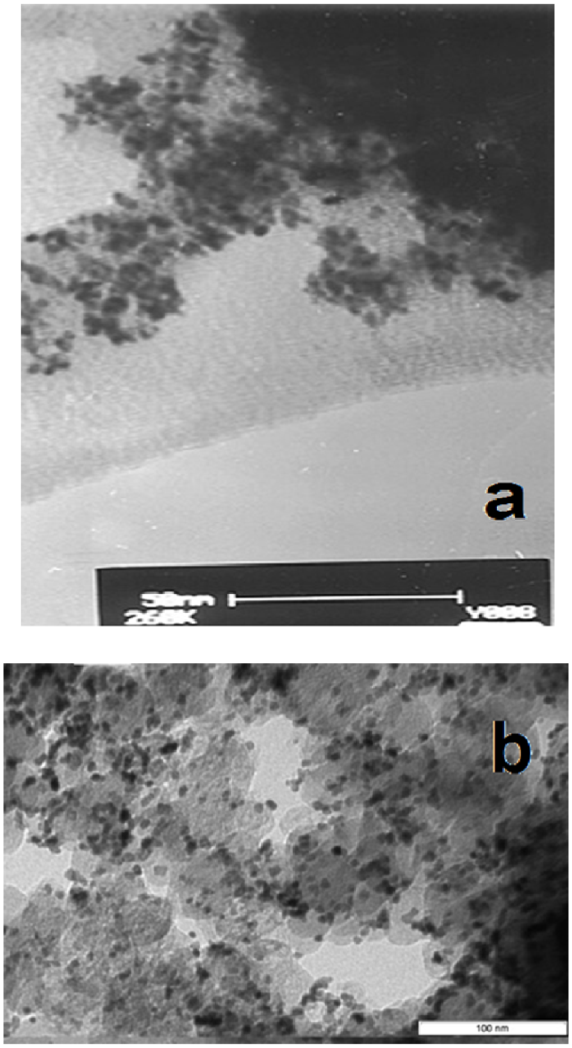

Figure 3. TEM images of Pt-Ni/Alumina a) and Pt-Ru/Alumina b) nanocomposites

Instrumentation

Electrochemical measurements were carried out with potentioglvanostate Wenking PGS 95. A standard three-electrode cell was employed. The GC electrode with 5 mm of diameter was used as the working electrode substrate. A saturated calomel electrode (SCE) and a gold electrode were used as the reference and counter electrodes, respectively. A 0.5 M solution of methanol prepared in 0.1 M H_2SO_4 served as the electrolyte. All experiments were done at scan rate of 50 mV s^{-1}. TEM images were obtained using a Philips CM120 transmission electron microscope with resolution 2.5A°. UV-Vis spectra were recorded on Jenway spectrometer with photodiode array detector.

Preparation of metale / carrier nanocomposites

In order to prepare metal nanoparticles, metal salts have been reduced chemically with $NaBH_4$. To have a complete reduction, NaBH4 concentration was used 10 times more than metal salts. In our procedure, a 25 ml metal salt aqueous solution (1 M H_2PtCl_6, 0.04 M $NiCl_2$ and 1 M $Ru(NO_3)_2$ or a mixture of metal salts aqueous solution) the mixture was stirred by a rotary (100 rpm) for 30 min, then a freshly prepared aqueous solution of $NaBH_4$ was added quickly to the mixture. The mixture was stirred for another 90 min to reduce the metal salts completely, then the mixture mixed with 10 ml 5% (w/v) Alumina . The products were kept at room temperature for characterization.

Electrode preparation

The GC working electrode with a definite area of 0.0714 cm^2 was polished with 0.05 mm alumina slurry to a mirror-finish. After washing with double-distilled water, it

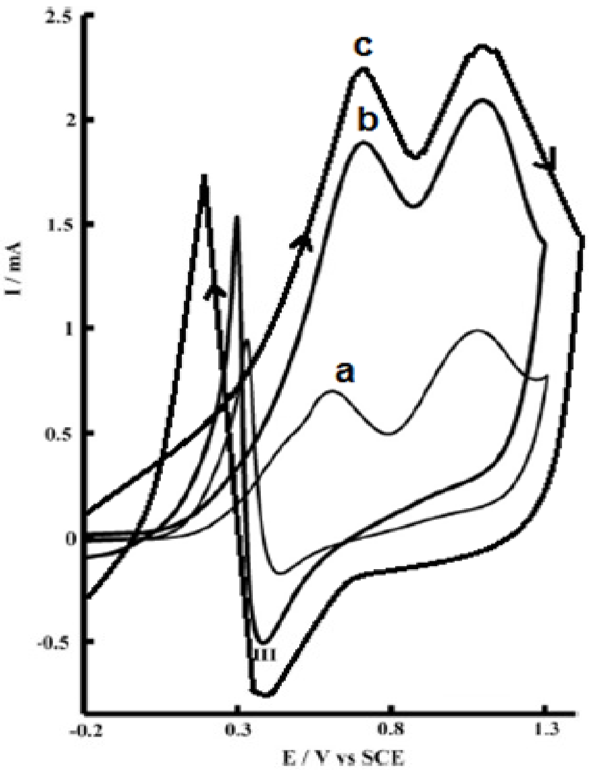

Figure 4. Cyclic voltammogram of 0.5M CH_3OH + 0.1M H_2SO_4 on a) Pt/Alumina /GC b)Pt-Ni/Alumina/GC c) Pt-Ru/Alumina/GC electrodes nanocomposites.

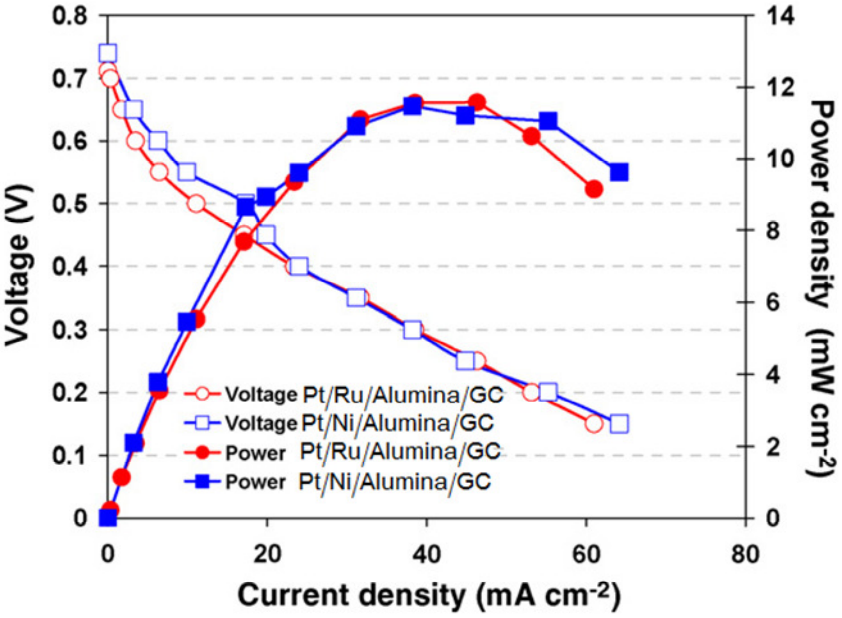

Figure 5. Voltage and power density of fuel cells.

was sonicated in water and absolute ethanol for about 5 min each. Next, the GC electrode was cleaned and activated in freshly prepared deoxygenated 1.0 $molL^{-1}$ H_2SO_4 by cyclic voltammetry between -1.5 and 1.5 V at a scan rate of 50 mV s^{-1} until a stable cyclic voltammetric profile was obtained and then it was used as the substrate for catalyst. The prepared catalyst suspension was spread by pipette onto the glassy carbon substrate. Evaporation of the solvent formed the deposited catalyst layer.

Fabrication and testing of complete fuel cells

Fuel cells were assembled using tubular cell design (Fig. 1) that consists of a perforated stainless steel tube. There was no preliminary hot-pressing procedure to prepare the membrane electrode assembly (MEA) as in other types of fuel cells, like PEMFC. Instead, the anode, membrane and cathode were placed around the hollow cylinder and clamped by a stainless steel grid, which provides good electrode/membrane interface. The electrode footprint area was 13 cm^2. The electrolyte with the fuel (i.e. 0.5M of CH_3OH + 0.1 M H_2SO_4) was then added to the cylinder. Electrochemical tests were performed on a single cell by polarising from open circuit potential to 0.1 V by stepping down the potential in steps of 50 mV. The electrochemical testing of the cells was performed using the versatile multipo- tentiostat VMP3 (Bio-Logic, France) or using an Arbin battery tester. All the experiments were carried out at room temperature.

RESULTS AND DISCUSSION

Characterization of nanocomposites

Fig.2 shows the UV-vis absorption spectra of platinum, nickel and ruthenium-Alumina nanocomposites. For platinum, nickel and ruthenium nanoparticles, there were no plasmon absorbance between 300 and 600 nm. (Huang et al., 2004).

Fig.3 shows the TEM images of nanocomposites. The presence of Pt, Ni and Ru nanoparticles is clearly observed. It is seen from TEM images that the overall size of the particles ranges from 2 to 7 nm and that particles exhibit fine spherical feature. It is clear the metal nanoparticles disperse better on the larger surface in the presence of Alumina.

Electrooxidation of methanol on modified glassy carbon with metal-Alumina nanocomposites

Fig.4 describes the anodic oxidation peaks on the smooth Pt and Pt based electrocatalysts which are attributed to methanol oxidation and forming Pt adsorbed carbonaceous intermediates, including CO and CO2 in the positive scan (PS). This adsorbed CO causes the loss of activity of the electrocatalyst. The reactions can be expressed as follows (Yen et al., 2007):

$Pt + CH_3OH \rightarrow Pt - CO_{ads} + 4H + 4e^-$ (1)

$CH3OH + H2O \rightarrow CO_2 + 6H^+ + 6e^-$ (2)

and additional oxidation of the adsorbed carbonaceous species to CO_2 according the bottom reaction in the negative scan (NS).

$Pt - CO_{ads} + H2O \rightarrow Pt + CO_2 + 2H^+ + 2e^-$ (3)

Therefore, the ratio of the anodic current in the PS to the anodic current in the NS reflects the ratio of the amount of methanol oxidized to CO_2 to the amount of CO. Hence, the ratio of the anodic current/cathodic current (I_{PS}/I_{NS}), can be used to describe the catalyst tolerance to carbonaceous species accumulation. Basically, a higher I_{PS}/I_{NS} value represents a relatively complete oxidation of methanol, producing CO_2, while; a low I_{PS}/I_{NS} ratio indicates poor oxidation of methanol to CO_2 during the PS and excessive accumulation of carbonaceous residues on the catalyst surface. In other words, this ratio essentially reflects the fraction of the electrocatalyst surface that is not poisoned by CO_{ads} and can be used to measure the catalyst tolerance to CO poisoning (Hsieh and Lin., 2009). Therefore, based on the above three key parameters (The peak current density in the PS, onset potential and the ratio of the I_{PS}/I_{NS}) the Pt-M (M= Ni and Ru) nanoparticles modified GCE showed an enhanced electrocatalytic activity towards the relatively complete methanol oxidation in comparison with Pt nanoparticles modified GCE (Razmi et al., 2008). As reported in the literature (Mathiyarasu et al., 2004), the effects of the alloying element (Ni and Ru) in the Pt based binary alloy on the electrooxidation reaction of methanol can be satisfactorily explained on the basis of (a) the bifunctional mechanism, which should consider adsorption properties of CO and OH surface species, (b) the electronic interaction between the alloying elementand Pt or synergistic role of Pt and metali in the catalysts (Hu et al., 2012) and (c) the increase in electrochemical active area due to the synergistic effect of the alloying element (Razmi et al., 2008) ; Mathiyarasu et al., 2004 ; Hu et al., 2012). In the present study the catalytic role of metal can be explained firstly by bifunctional mechanism, according to this theory (Hsieh and Lin., 2009), (Watanabe and Motoo, 1975), an efficient catalyst favors CO adsorption on Pt and OH_{ads} formation takes place on the second metal. Hence, the binary combination yields the best overall activity for methanol oxidation. Therefore, CO adsorption mainly occurs on Pt, while OH_{ads} species easily interact with metal surface (Wang et al., 2006).

$M + H_2O \rightarrow MOH + H^+ + e^-$ (4)

$MOH_{ads} + PtCO_{ads} \rightarrow CO_2 + Pt + M + H^+ + e^-$ (5)

And secondly, by increase in electrochemical surface area due to the synergistic effect of the alloying element in the Pt-M alloy (Flower like nanoparticles of the Pt-Ni) (Habibi, 2011).

Fuel cell testing

Tubular fuel cells were assembled using membrane electrode assembly (MEA) comprising of nano-particulate Pt/M/Alumina/GC (M = Ru and Ni) as the anode, the anionic membrane and silver-based catalyst AC65 as the cathode. The latter functioned as air-breathing without any auxiliary facilities. In order to gain an insight of different phenomena arising at different electrode interfaces, a reference electrode was inserted in the tubular cell. The cell was polarised from open circuit voltage to 0.1 V in steps of 50 mV. The data is summarized in Fig. 5. Surprisingly, the current density measured on both systems was found to be fairly similar with a maximum power density of 12 mW cm^{-2}.

CONCLUSION

In this work, P-M-Alumina (M = Ni, Ru) nanocomposites were successfully synthesized. The GC/Pt/Ni/Alumina, and GC/Pt/Ru/Alumina electrodes were prepared as active electrocatalysts for oxidation of methanol. Our results showed that the addition of Ru and Ni nanoparticles into Pt catalyst and use of a more porous matrix of Alumina can considerably improve the electrode performance for methanol electrooxidation. The activity of GC/Pt/Ru/Alumina for methanol electrooxidation in acid solution is higher than that of GC/Pt/Ni/Alumina catalyst with respect to the higher current density of methanol oxidation and also higher electrochemically active surface area.

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