دانشگاه تربیت دبیر شهید رجایی
دانشکده علوم پایه

چهارمین سمینار
پیل سوختی ایران
4th Iranian Fuel cell seminar
سوم و چهارم آذر ماه ۱۳۸۹
November 24 & 25 ,2010

www.iranecs.ir/fuelcellseminar

Carbon-Ceramic Supported Bimetallic Pt-Ni Nanoparticles as Catalysts for Formic acid

Biuck Habibi* **and Nasrin Delnavaz**
Electroanalytical Chemistry Laboratory, Faculty of Sciences, Department of Chemistry, Azarbaijan University of Tarbiat Moallem, Tabriz, Iran
B.Habibi@azaruniv.edu

Abstract

Pt-Ni nanoparticles supported on carbon-ceramic electrode (Pt-Ni/CCE) are prepared by an electrodeposited process. The catalysts are characterized by Scanning electron microscopy, Energy-dispersive X-ray spectroscopy (EDX) and cyclic voltammetry. The results show that the Pt-Ni nanoparticles dispersed uniformly on carbon-ceramic electrode. The Pt-Ni/CCE catalysts have higher electrocatalytic activity for formic acid oxidation than a comparative Pt/CCE and show great potential as less expensive electrocatalyst. The effect of some experimental factors was studied and optimum conditions were suggested. Finally, the long-term stability of the modified electrode has also been investigated. These results indicate that the system studied in the present work is the most promising system for use in Direct Formic Acid Fuel Cells (DFAFCs).

Keywords: Platinum-Nickel nanoparticles, Electrooxidation, Formic acid

1. Introduction

During the past 20 years, direct methanol fuel cells have been widely studied and considered as possible power sources for the portable electronic devices and electric vehicles. These fuel cells offer a variety of benefits such as high specific energy and the ready availability and portability of methanol. On the other hand, the problem of methanol ‘crossover’ from the anode to the cathode through membrane leads to low system efficiency. Methanol crossover prevents utilization of high concentration of methanol; the limits generally less than 2 M. As an attractive candidate to replace methanol, formic acid (FA), a non-toxic, non-explosive and non-flammable liquid at room temperature has considerable advantages [1]. The feasibility of direct formic acid fuel cells (DFAFCs) based on proton exchange membranes has been demonstrated by Masel and co workers [1, 2]. Hsing and co workers [3] have also reported that the rate of fuel crossover can be reduced by a factor of 5 and thus a higher performance can be obtained when FA is used in place of methanol under the same conditions.

One of the key problems in proton exchange membrane fuel cells is the development of anodic materials with high electroactivity towards the oxidation of FA and methanol. It is well known that platinum is an effective electrocatalyst for these oxidations. However, Pt is also highly sensitive to CO poisoning: the catalyst surface is progressively poisoned by the adsorbed CO, which is formed as a result of the stepwise dehydrogenation of these oxidants in oxidation reaction [4]. Poisoning CO_{ad} species can be oxidatively removed from the Pt surface through a Langmuir-Hinshelwood-type surface reaction with neighboring OH_{ad} species electrosorbed from water at more positive potentials. Thus, alloying of Pt with oxophilic metals enables electrochemical dissociation of water on non noble metal sites at more negative potentials compared to pure Pt and, therefore, allows electrocatalytic oxidation of adsorbed CO at lower anodic overpotentials. In order to improve the electrocatalytic performance of the Pt catalyst, the Pt-based bimetallic catalysts, such as Pt-Au [5], Pt-Ru [6], Pt-Bi [7] and Pt-Ir [8], Pt-Pb [9], Pt-Sb [10], Pt-Os [11], Pt-Pd [12], Pt-Fe [13], Pt-Sn [14] and Pt-Ag [15] have been investigated. However, to the best of our knowledge, Pt-Ni bimetallic catalysts for FA electrooxidation have not been reported yet.

In this work, we have prepared CC supported platinum-nickel nanoparticles by a two- step procedure: (I) the CC substrate was produced by using sol-gel technique and (II) platinum-nickel nanoparticles were precipitated electrochemically on the surface of CC substrate and the resulting electrode was referred as Pt-Ni/CCE. After surface and structural characterizations of the Pt-Ni/CCE, the electroactivity of Pt-Ni/CCE towards the formic acid oxidation in 0.1 M H_2SO_4 solution was evaluated by cyclic voltammometric and chronoamperometric measurements and the obtained results were compared with those obtained on the smooth platinum and platinum particles CC electrodes. It was found that Pt-Ni/CCE was catalytically more active than smooth platinum and platinum particles supported CC electrodes. The effect of some experimental factors was studied and optimum conditions were suggested. Finally, the long-term stability of modified electrode has also been studied.

2. Experimental

2.1. Chemicals

Methyltrimethoxysilane (MTMOS) was from Fluka. Formic acid, methanol, $H_2PtCl_6.5H_2O$, $NiCl_2$, HCl, H_2SO_4 and graphite powder of high purity were obtained from Merck. All solutions were prepared with double distilled water.

2.2. Procedure of Pt-Ni/CC preparation

2.2.1. CCE preparation

The sol-gel processing method was used for fabricating CC substrate according to the following procedure: The amount of 0.9 ml MTMOS was mixed with 0.6 ml methanol. After addition of 0.6 ml HCl 0.1M as catalyst, the mixture was magnetically stirred (for about 15 min) until it produced a clear and homogeneous solution. Then, 0.3 g graphite powder was added and the mixture was shaken for another 5 min. Subsequently, the homogenized mixture was firmly packed into a Teflon tube (with 3 mm inner diameter and 10 mm length) and dried for at least 24 h at room temperature. A copper wire was inserted through the other end to set up electric contact. The electrode surface was polished with 1500 emery paper and rinsed with water.

2.2.2. Pt-Ni/CCE preparation

Electrochemical deposition is an efficient method for the preparation of metal particles. It is widely used with different strategies/methodologies, such as potential step deposition, cyclic voltammetry, double-pulse and galvanostatic methods. Among these, potential step deposition provides a tool to fine-tune the amount of the metal deposited, the number of metallic sites and their size. Electrodeposition of platinum tin alloy on CC substrate was performed potentiostatically from an aqueous solution of 0.1M H_2SO_4 containing H_2PtCl_6 and $NiCl_2$.

2.3. Instrumentation

The electrochemical experiments were carried out using an AUTOLAB PGSTAT-30 (potentiostat/galvanostat) equipped with a USB electrochemical interface and a driven GEPS software was used for electrochemical experiments. A conventional three electrode cell was used at room temperature. A disc of CC/Pt (3 mm diameter) was used as a working electrode. A saturated calomel electrode (SCE) and a platinum wire were used as the reference and auxiliary electrodes, respectively. JULABO thermostat was used to control cell temperature at 25°C. Scanning Electron Microscopy (SEM) and Energy-Dispersive X-ray spectroscopy (EDX) were performed on a LEO 440i Oxford instrument. Chemical composition analysis of the catalyst was carried out on an energy dispersive X-ray (EDX) analyzer attached to the same device.

3. Results and discussion

3.1. Characteristics of Pt-Ni/CCE

To understand the electrochemical activity of the Pt-Ni/CCE, the cyclic voltammetric responses of the Pt-Ni/CCE was recorded in the potential range between -0.3 and 1.3 V at a scan rate of 50 mV s^{-1}. Figure 1 shows the CV of the Pt-Ni/CCE in 0.1 M H_2SO_4 solution. Although the typical Pt-peaks for the hydrogen under-potential deposition (H_{udp}) and the oxidation of hydrogen (H_{oh}) are present on the Pt-Ni/CCE, they become ill-shaped compared to the Pt/CCE and pure Pt [16]. Furthermore, Figure. 1 shows that both oxidation and reduction current densities of CV on the Pt-Ni /CCE are much higher than those on the polycrystalline Pt.

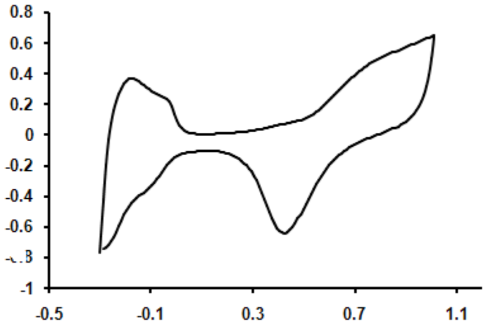

Figure 1. Cyclic voltammogram of Pt-Ni/CCE in 0.1M H_2SO_4 at a scan rate of 50 mV s^{-1}.

In order to surface characterization of the Pt-Ni/CCE catalyst, the micrograph of CC substrate and Pt-Ni/CCE has been investigated by SEM and the corresponding results were shown in Figure. 2. Image A shows the structure of the bare CC surface immediately after polishing with emery paper grade 1500. As seen in this image the surface is dense, scaly and has a high porosity. The average pore size of CC substrate is 0.2 µm. Image B shows the SEM micrograph of the CC surface after platinum-Nickel deposition. As seen, the Pt-Ni nanoparticles are cluster (Flower like) and separate and the surface coverage is almost uniform without any holes and deficiency. Most likely, the particulate structures of platinum in this image are not the individual platinum crystallites. They are, most probably, clews consisting of crystallite aggregates.

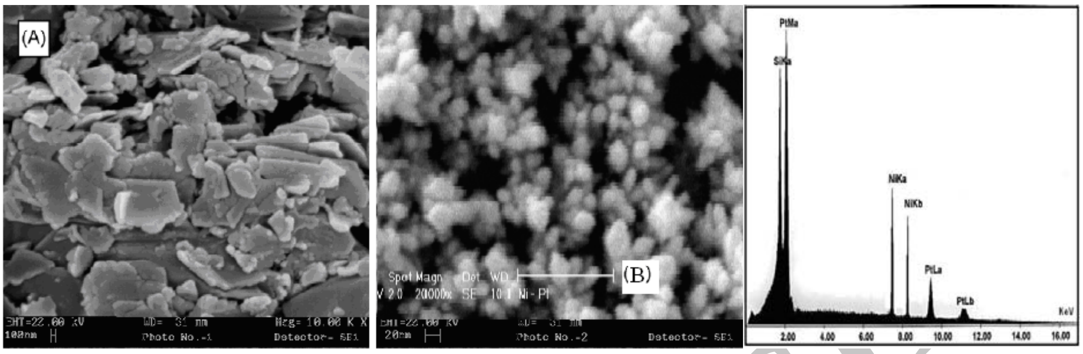

Figure 2. SEM images of (A) CCE surface, (B) Pt-Ni/CCE and EDX analysis of Pt-Ni.

The EDX data for the Pt-Ni nanoparticles on CCE was acquired simultaneously to the SEM data, and is shown in figure. 2. The obtained chemical composition is: wt% Pt and Ni are 49 and 46.6, respectively and remaining percentages correspond to the other elements such as Si.

3.2. The electrocatalytic oxidation of FA

Fig. 3 shows the CVs of the Pt-Ni/CCE in a 0.5M FA + 0.1M H_2SO_4 solution. The CV of Pt-Ni/CCE shows the usual characteristics of pure platinum except that both for forward and reverse scan directions the oxidation currents of FA on the Pt-Ni/CCE are significantly higher than on the platinum. It can be seen from voltammogram of FA oxidation on the Pt-Ni/CCE that the reaction commences in the hydrogen region and proceeds slowly in the positive direction, and then reaches a plateau at ca. 0.21 V. At potentials with more than ca. 0.5 V, the reaction becomes accelerated and maximum rate at ca. 0.75 V occurs. A rapid increase in current at potentials more than ca. 0.95 V is assigned to oxygen evolution. Upon reversing the potential sweep, a very steep increase of the reaction rate at ca. 0.5 V develops and a maximum current is observed at ca. 0.35 V. After that, the current gradually decreases but the reaction rate is still faster than in the forward scan.

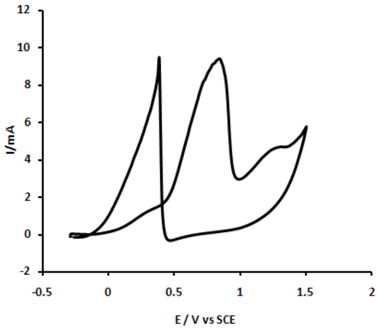

Figure 3. Cyclic voltammogram of 0.5 M FA on the Pt-Ni/CCE in 0.1M H_2SO_4 at a scan rate of 50 mV s^{-1}.

This large anodic peak in the reverse scan is attributed to the removal of the incompletely oxidized carbonaceous species formed in the forward scan. It has been widely accepted in the literature that FA is oxidized to CO_2 via a dual path mechanism, which involves a reactive intermediate (main path, dehydrogenation) and adsorbed CO as a poisoning species (parallel path, dehydration). In one pathway, direct oxidation of FA is said to occur whereas in the other pathway, FA is oxidized to CO, which in turns must be removed by activating water. While the net reaction is the same in both of the pathways, the water dissociation reaction is rather difficult. The OH_{ads} formed by the dissociation of water molecules on platinum surface aids in removing the adsorbed surface poison CO_{ads} by oxidizing it. But indeed this process is very intricate, as a higher potential is required for water activation (>0.5V) on platinum surfaces. And the second metal has very important in the preparation of the OH_{ads} formed by the dissociation of water molecules. It can be seen from the results that the electrocatalytic activity of platinum-nickel nanoparticles decorated CC substrate towards FA oxidation [$I_{p(PGPS)}$=142.8 mA/cm^2(A_g)] was greatly improved than those with platinum nanoparticles on CCE [$I_{p(PGPS)}$=74.43 mA/cm^2(A_g)] [16] and platinum [$I_{p(PGPS)}$=8.57 mA/cm^2(A_g)]. This is rising from the role of second metal (nickel) in the providing of OH_{ads}.

3.3. Chronoamperometric study of oxidation of FA

Figure 4 shows the typical chronoamperometric response curves of FA in $0.1H_2SO_4$ on Pt-Ni/CCE and platinum as the working electrodes. It was found that the current observed from chronoamperograms was in good agreement with the current observed from cyclic voltammetry. A further investigation was done to find out the effect of applied potential in chronoamperometric response of oxidation of FA at the Pt-Ni/CCE electrode. Chronoamperometric data of the Pt-Ni/CCE were recorded by potential steps from 0 mV for 60 s to the various potentials for 500 s. The current-time transient for the FA oxidation at different anodic potentials shows that the steady-state current at the ending time (t=500 s) increases with an increase in applied potential. Phenomenologically, the oxidation current increases slowly with time at 200 and 300 mV, while at higher potentials the current increases sharply during short times and then decreases slowly at longer times. This may be caused by the CO-poisoning effect which results in deactivation of the catalyst surface and blocks further oxidation of FA.

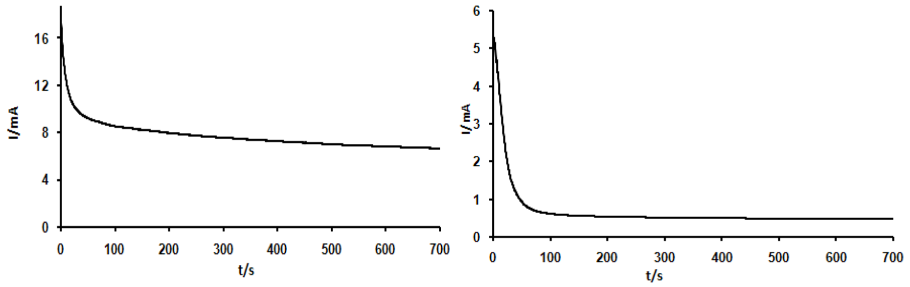

Figure 4. Chronoamperometric curves of 0.5M FA electro-oxidation in 0.1M H_2SO_4 on the Pt-Ni/CCE (left) and smooth Pt (right) electrodes, respectively.

3.4. Parameters affecting the anodic peak currents of FA oxidation

3.4.1. Effect of platinum/nickel ratio

As reported in literature [14], the electrochemical catalytic activity of platinum-nickel nanoparticles strongly depends on the ratio of deposited platinum/nickel nanoparticles and the conditions of deposited bimetallic electrocatalyst (Pt-Ni) are very critical in order to obtain an optimized electrode. Figure 5 (Left) reports the values of the maximum current for the electrooxidation of formic acid (0.50 M in 0.10 M sulfuric acid) obtained during a voltammogram recorded at 50 mV s^{-1} against the concentration of Ni ion in loading solution. The current decreases abruptly after a slight increase for very low concentrations of Ni. We assume this increase to a progressive formation of Pt-Ni nanoparticles with larger surface area, whereas, the decrease in peak current corresponds most probably to the agglomeration of formed nanoparticles to form clusters with lower surface area. The obtained composition ratio via EDX analysis is in good agreement with the ratio of concentration of each metal in solution.

3.4.2. Effect of FA concentrations

In order to evaluate the capacity of Pt-Ni/CCE for electrooxidation of FA, the effect of concentration of this compound on the corresponding anodic peaks currents was investigated by CV. According to experimental data, the peak current of FA was increased by increasing of concentration of this compound, and reached a nearly constant value for concentrations higher than 1.5M for FA. We assume this effect caused by saturation of active sites at the surface of electrode.

3.4.3. Effect of electrolyte concentration

The effect of H_2SO_4 concentration on the peak current related to the electrooxidation of FA at Pt-Ni/CCE has been investigated by cyclic voltammetry. The variation of peak current obtained for FA oxidation was plotted against H_2SO_4 concentration in Figure 5 (Right). The peak current of FA oxidation increases with the increase of H_2SO_4 concentration to 0.1M, and then it remains constant for the optimum H_2SO_4 concentration range 0.10-0.18M. Further increase in H_2SO_4 concentration depressed the anodic peak current. In high concentrations of H_2SO_4, the dissociation of acid decreases and causes the solution conductivity to be reduced.

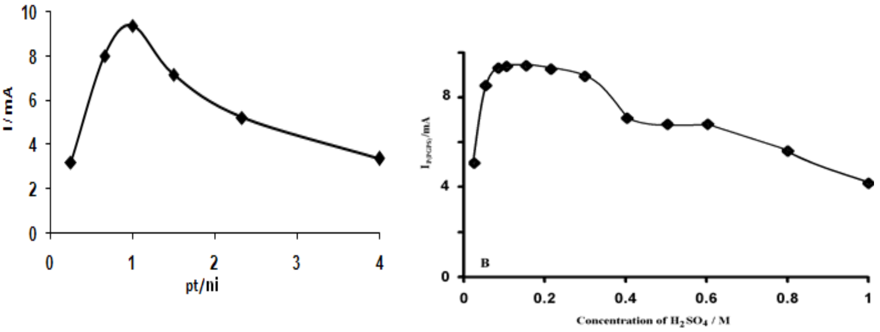

Figure 5. (Left) Plots of anodic peak current in the electrooxidation of 0.5 M FA as a function of ratio of Pt/Ni on the CC substrate in 0.1 M H_2SO_4. (Right) Variation of anodic peak current in PGPS in the electrooxidation of 0.5 M FA vs. H_2SO_4 concentration at scan rate 50 mV s^{-1}.

3.5. Long-term stability of the platinum nanoparticles decorated CC substrate

In practical view, long-term stability of the electrode is important. The long-term stability of Pt-Ni/CCE was examined in 0.1M H_2SO_4 solution containing 0.5M FA (Figure 6). It can be observed that the anodic current remains constant with an increase in the scan number at the initial stage. In the case of FA oxidation using Pt-Ni/CCE, the anodic current starts to decrease after 50 numbers of scans. The peak current of the 300th scan is about 92.5% than that of the first scan. In general, the loss of the catalytic activity after successive number of scans may result from the consumption of FA during the CV scan. It may also be due to poisoning and the structure change of the platinum-tin nanoparticles as a result of the perturbation of the potentials during the scanning in aqueous solutions, especially in presence of the organic compound. Another factor might be due to the diffusion process occurring between the surface of the electrode and the bulk solution. With an increase in scan number, FA diffuses gradually from the bulk solution to the surface of the electrode. After the long-term CV experiments, the Pt-Ni/CCE was stored in water for a week; then FA oxidation was carried out again by CV, and excellent catalytic activity towards oxidation of FA was still observed. This indicates that the Pt-Ni/CCE composites prepared in our experiment have good long-term stability and storage properties.

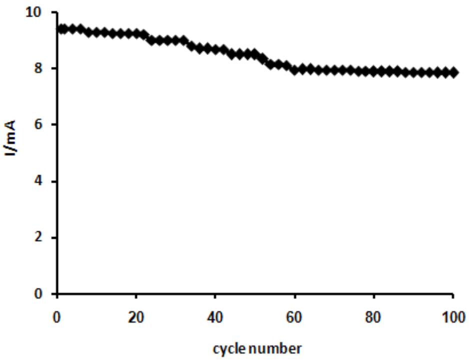

Figure 6. Long-term stability of Pt-Ni/CCE in 0.1 M H_2SO_4 and 0.5 M FA vs. number of scans [scan rate (50 mV s^{-1})].

4. Conclusions

A bimetallic platinum-nickel nanoelectrocatalyst with the platinum-nickel atomic ratio in surface layer 1:1 is synthesized by depositing on highly prose carbon-ceramic from a solution of the corresponding metals. Formic acid electrooxidation at this catalyst was studied. It was shown that the catalytic activity of the synthesized catalyst exceeds that of platinum nanoparticles (alone) on carbon-ceramic and smooth Pt electrodes. The catalyst may be perspective as anodic material for applications in direct formic acid fuel cells.

Acknowledgment

The authors gratefully acknowledge the research council of Azarbaijan University of Tarbiat Moallem for financial support.

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