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The effect of polypyrrole nanowires on electroactivity of platinum nanoclusters in methanol oxidation

Akram Maghsodi, Mostafa Dehghani Mobarakeh*
Energy Research Center, Renewable Energy Department, Research Institute of Petroleum Industry (RIPI),
P.O. Box 14665-1998, Tehran, (IRAN)
E-mail : akram_maghsodi@yahoo.com; dehghanim@ripi.ir

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ABSTRACT

In this work, first, polypyrrole (PPy) nanowires were deposited on Glassy Carbon Electrode (GCE) by chronoamperometry (PPy/GCE). Then Pt nanoclusters were dispersed on the as formed electrode by Cyclic Voltammetry (CV) methode (PPy–Pt/GCE). Cyclic Voltammetry and chronoamperometry techniques were employed for investigation of electrocatalytic activities toward methanol oxidation reaction (MOR). The results showed, PPy–Pt nanocomposites have a higher surface area and better electrocatalytic activity as compared to pure Pt modified electrode. This difference could be attributed to high dispersion of Pt nanoclusters in PPy nanowires and synergic effect of the Pt and PPy nanowires. It appeared that, PPy–Pt nanocomposite could be an alternative anode material for direct methanol fuel cells.

KEYWORDS

Polypyrrole nanowire;
Pt nanocluster;
Methanol electrooxidation reaction;
Direct methanol guel vell.

INTRODUCTION

During the past decades, direct methanol fuel cell (DMFC) has been widely investigated. It has significant advantages for powering portable applications since it does not require a separate hydrogen generation system and has high energy density[1]. The most active catalyst for methanol oxidation reaction in DMFCs is Pt or Pt-based alloys in acidic solution. The DMFC has at least two problems to be suitable for practical uses: (1) it requires expensive electrocatalysts such as Pt for the methanol oxidation (2) the active sites of the electrocatalysts are poisoned by the adsorption of reaction intermediates such as CO[2,3].

The catalytic composites of Pt/Ru[4], Pt/Ru/Fe[5], Pt/Pd[6], Pt/Ru/Ni[7] and Pt/Ru/W[8] have been developed for DMFCs, in order to reduce the poisoning effect of the catalyst and thereby improve the catalytic performance. However, the costs of these electrocatalyst materials are often expensive. Application of conductive polymers is a promising strategy for decreases these problems. Conducting polymers appeared to be suitable host matrix for dispersing metallic particles in fuel cells, owing to their unique electronic properties. The composite of conducting polymer–metal nanoparticles permits a facile flow of electronic charges through the polymer matrix in electrochemical processes[9]. Among the numerous conducting polymers, Polypyrrole (PPy) is one of the best candidates because PPy nanowires have large surface area, highly electronic conductivity and charge transport properties. The PPy nanowires possess porous structure, which is suitable to accommodate a dispersed catalyst and remarkably reduce the cost of fuel cells. The incorporation of a catalyst into the porous PPy nanowire matrix not only increases the specific area of the catalyst material but also, enhances the tolerance of the anode catalyst to CO poisoning[10].

Here we reported the catalytic activity of PPy–Pt/GCE in the MOR. The PPy–Pt/GCE showed excellent catalytic activities toward MOR relative to pure Pt modified electrode. Moreover, the content of Pt metal in the catalyst was remarkably reduced, and thereby the cost of prepared catalyst was decreased.

EXPERIMENTAL

Chemicals and reagents

Pyrrole was obtained from Merck and purified by distillation under nitrogen atmosphere. $K_2Pt Cl_6$ and methanol were obtained from Merck. All other Chemicals were of analytical grade and were used without further purification.

Apparatus

Electrochemical measurements were carried out using an Autolab potentiostat / galvanostat PGSTAT30. A conventional three-electrode cell was used with Ag/AgCl sat. KCl as reference electrode, a Pt wire as counter electrode, a glassy carbon electrode (GCE, 0.07065 cm^2) as working electrode. All experiments were carried out at ambient temperature in acidic media.

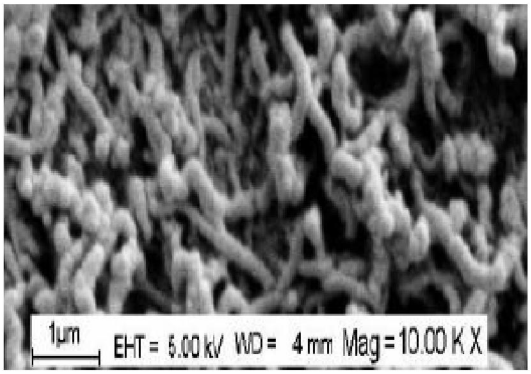
Preparation of electrodes

Prior to modification, the glassy carbon electrode with a diameter of 3mm was polished with 0.05 μm alumina powder on polishing cloth and rinsed thoroughly with distilled deionized water. The PPy was electrochemically deposited at a constant potential of 0.80 V for 120 s in an aqueous solution of 0.1 M $LiClO_4$ and 0.1 M carbonate containing 0.15 M pyrrole. Freshly prepared PPy film electrodes were usually immersed in 10% $HClO_4$ solution for 12 h in order to remove any CO_3^{-2} ions. The PPy nanowires modified electrode was obtained and denoted as PPy/GCE. Then PPy/GCE was treated by CV in 0.5 M H_2SO_4 + 2.0 mM K_2PtCl_6 in the potential range from 0.4 to -0.2 V at 50 $mV.s^{-1}$ for embedding Pt nanoclusters in PPy nanowires. The PPy–Pt nanocomposite modified electrode was obtained and denoted as PPy–Pt/GCE. For comparison, the same Pt deposition process was conducted at bare GCE and denoted as Pt/GCE. The optimal cycle number was achieaved around 30.

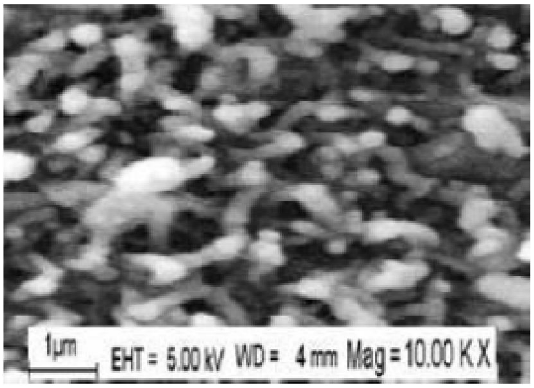
REASULTS AND DISCUSSION

Characterization of PPy/GCE and PPy-Pt/GCE

Scanning electron microscopy (SEM) images of the synthesized PPy nanowires and PPy–Pt on glassy carbon electrode were shown in Figure 1. Figure 1(a) shows the sponge-like nano-matrix consisted of PPy nanowires on GCE surface with a diameter of about 90 nm. Figure 1(b) shows the morphology of the PPy–Pt nanocomposite on the GCE. The diameter of Pt nanoclusters in PPy–Pt/GCE was estimated around 100-140 nm.



(a)



(b)

Figure 1 : SEM images of (a) the PPy nanowires and (b) the PPy–Pt nanocomposite on the bare GCE.

CV_S curves for PPy–Pt/GCE in 0.5 M H_2SO_4 solution saturated N_2 were shown in Figure 2. The presence of oxidation/reduction peaks are due to formation of Pt nanoclusters on the electrode. A pair of current peaks between -0.15 and +0.10 V presents the hydrogen adsorption and desorption at Pt particles. The electrochemical active surface area (EAS, $m^2.g^{-1}$) of the deposited Pt catalyst can be measured by integrating Coulombic charge for hydrogen adsorption or desorption (Q_H) on the CV curves in N_2-purged 0.5 M H_2SO_4 solution. The EAS was obtained according to the following equation[11]:

$$\mathbf{EAS = \frac{Q_H}{0.21\,[Pt]}}$$

Where the [Pt] is the Pt loading ($mg.cm^{-2}$), Q_H is the charge for H_2 adsorption or desorption ($mC.cm^{-2}$) and 0.21 is the charge required to oxidize a monolayer of H_2 on smooth Pt. The calculated EAS was 32 and 21 $m^2.g^{-1}$ for the PPy–Pt/GCE and Pt/GCE respectively. PPy–Pt/GCE showed much higher EAS than Pt/GCE, which may be attributed to the high surface area of PPy nanowires and smaller Pt nanoclusters dispersed in PPy nanowires.

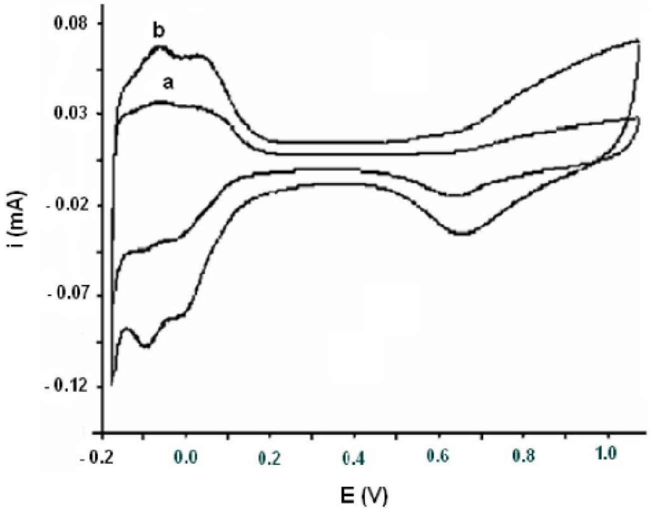


Figure 2 : CV_s in 0.5 M H_2SO_4 solution saturated N_2 at the (a) Pt/GCE and (b) PPy–Pt/GCE with 50 $mV.s^{-1}$ scan rate

Electrocatalytic activity of methanol oxidation reaction

CV and chronoamperometry techniques were used for evaluation of MOR reactivity. The electro-oxidation of methanol on PPy–Pt/GCE and Pt/GCE was studied by CV in 0.5 M H_2SO_4+0.5 M CH_3OH aqueous solution at 50 mv s^{-1} and the resulting CV_s are shown in Figure 3. In the forward scan, where as an anodic peak at 0.66 V with a peak current density (I_p) of 17 $mA.cm^{-2}$ (curve a) is related to methanol oxidation in PPy–Pt/GCE electrode, an anodic peak appeared at 0.48 V in the reverse scan was attributed to the removal of incompletely oxidized carbonaceous species generated in the forward scan. These carbonaceous species are mostly in the form of linearly bonded Pt=C=O[12]. For comparison, the CV at the Pt/GCE was shown in curve b. The voltammogram of methanol oxidation at Pt/GCE was very similar to that of PPy–Pt/ GCE, and the two oxidation peaks appear at 0.74 and 0.52 V.

The peak current density at Pt/GCE is much smaller than that of PPy- Pt/GCE. The enhanced electrocatalytic activities at PPy–Pt/GCE can be assigned to the uniform dispersion of Pt clusters in the PPy nanowires and the synergic effect of the PPy–Pt composite. The effective dispersion and utilization of Pt clusters in the high electron conductivity PPy nanowires inhibits the formation of strongly chemisorbed and thereby decreases the Pt catalyst surface poisoning, which are a benefit to enhance the electrocatalytic performance toward methanol oxidation. The catalyst tolerance to carbonaceous species accumulation can be described by the ratio of the forward anodic peak current (I_f) to the reverse anodic peak current (I_b).

Highly I_f/I_b ratio indicates methanol is efficiently oxidized to CO_2 and a little accumulation of carbonaceous residues on the catalyst surface[13].

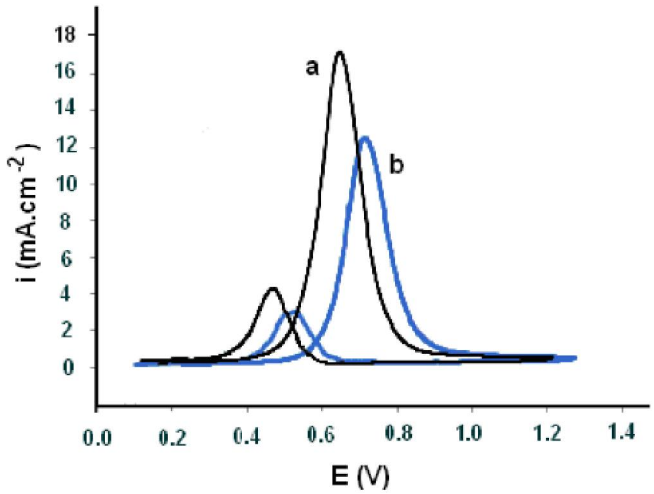


Figure 3 : CVs of PPy–Pt/GCE (a) and Pt/GCE (b) in nitrogen saturated 0.5 M H_2SO_4 and 0.5 M CH_3OH aqueous solution at 50 $mV.s^{-1}$ scan rate

Figure 4 shows, chronoamperometric curves measured at different potentials 0.75, 0.70, 0.65 and 0.55 V at the PPy–Pt/GCE for 1 h. As can be seen, the largest current has achieved at 0.65 V and the current decreased with passing of time. The result is in good agreement with CV result of methanol oxidation.

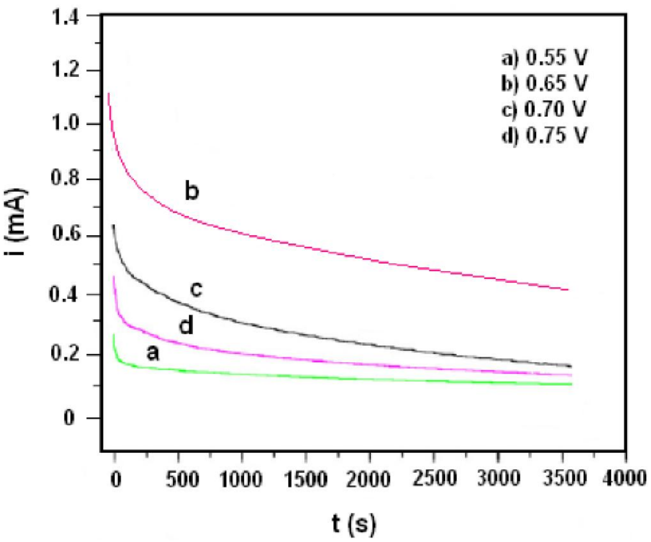


Figure 4 : Chronoamperometric curves for the PPy–Pt/GCE at 0.75, 0.70, 0.65 and 0.55 V in 0.5 M H_2SO_4+0.5 M CH_3OH aqueous solution.

In order to compare the performance of the PPy–Pt/GCE and Pt/GCE towards the MOR, chronoamperometry tests were done in 0.5 M H_2SO_4 solution containing 0.5 M methanol at 0.65 V for 1 h, as shown in Figure 5. In the initial period of time, the current decreases probably due to the formation of intermediate species, such as CO_{ads}, CH_3OH_{ads}, and CHO_{ads} for both the electrodes during the methanol oxidation reaction[14]. After long time operation, although the current is gradually decayed, but the initial and limiting currents of PPy-Pt/GCE are higher than Pt/GCE throughout all the ranges up to 3600 s. So, it indicates that the PPy-Pt nanocamposite is more active than the Pt nanoparticles for methanol electro-oxidation, as is consistent with the CV results.

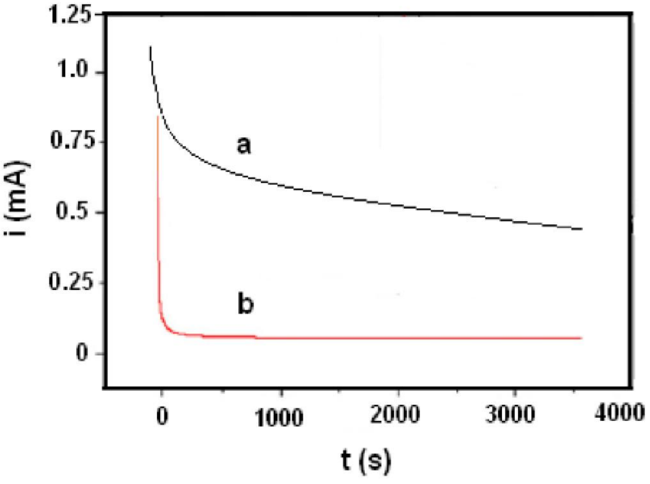


Figure 5 : Chronoamperometric curves of the PPy-Pt/GCE (a) and the Pt/GCE (b) at 0.65V in 0.5 M H_2SO_4 + 0.5 M CH_3OH aqueous solution.

CONCLUSION

In this work, we deposited Pt clusters in PPy nanowires and formed a PPy–Pt nanocomposite on glassy carbon electrode surface. The enhanced electrocatalytic activity was achieved by PPy–Pt composite in relative to pure Pt modified GCE toward MOR reaction. The advantage of the prepared PPy–Pt/GCE was attributed to the 3D structure of the composite, high dispersion of Pt nanoclusters in large surface area of PPy nanowires and synergic effect between Pt and PPy nanowires. So, it appeared that, this electrode can be an alternative anode material for direct methanol fuel cells.

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