The Catalytic Effect of Polypyrrole/Pt-Cu on Oxygen Reduction Reaction

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This paper studies the electrochemical properties of ppy/Pt-Cu composite for oxygen reduction reaction (ORR) and compares it to the highly porous ppy/Pt-Cu catalyst, which can be synthesized by galvanostatic method (ppy/Pt-Cu(GS)). The results of the polarization, rotating disk electrode and electrochemical impedance tests are discussed to determine the electrochemical properties of the catalysts. According to the results, ppy/Pt-Cu(GS) catalyst is more active toward ORR compared to ppy/Pt-Cu catalyst. The Rotating disk electrode data indicates four-electron transfer mechanism for this catalyst.

Keywords: Polypyrrole, Nano Platinum, Fuel cell.

1. INTRODUCTION

In the recent years, special attention has been paid to Fuel Cells as clean sources of energy. Proton Exchange Membrane fuel cells can be more interesting than other types of fuel cells due to their high efficiency and low working temperature. Oxygen Reduction Reaction (ORR) is the main reaction in Fuel cells. For increasing the rate of this reaction, various catalysts have been investigated such as monometallics [1-5], bimetallics [6-16], ternary systems [17,18], oxides [19-21] and other types of catalysts [22]. Platinum is the dominant catalyst used in fuel cells because of its high efficiency and stability although it is costly. Considering the cost of platinum, alloying platinum with transition metals, using Platinum in form of nanoparticles and increasing contact surface area between catalyst and electrolyte would be considered as solutions for lowering the platinum content of cathode catalyst.

There are various methods for preparation of catalysts, such as chemical reduction [3,8,5,6,11], colloidal [1,2,7], sputter depositor [4,10] and electrochemical method [8,9]. Choosing the proper

method is of utmost importance because all these methods have some advantages and disadvantages which can affect the final structure and efficiency of the catalysts.

Application of nanosized catalyst particles is one of the promising solutions for creating higher surface area and consequently more efficient catalysts. More catalytic sites can be achieved by using catalysts in form of nanoparticles. More catalytic sites can increase the rate of oxygen reduction.

With the help of conductive polymers, especially Polypyrrole, porous polymer based matrix for nano-sized catalyst were investigated [2,23]. Polypyrrole is a conductive polymer, which can act as a good catalyst for ORR and a good matrix for accommodating Pt nano particles. Polypyrrole can be used for creating the cathode of low temperature fuel cells, thus higher contact area can be achieved and performance can be improved.

Further improvement as well as lowering the cost can be obtained by adding Copper and Platinum particles to ppy to make a bimetallic catalyst. Therefore, the aim of this paper is to study the catalytic effect of this composite on ORR.

In the present study, nanoparticle of catalysts were dispersed within the Polypyrrole matrix and electrochemical properties of ppy/Pt-Cu fabricated by two methods of cyclic voltammetry and Galvanostatic synthesis were compared. The Combination of polypyrrole and Pt-Cu bimetallic alloy in galvanostatic method increased the catalytic activity.

2. EXPERIMENTAL

Two types of polypyrrole catalyst containing Pt-Cu particles were made with different methods of preparation. The catalysts were prepared on the surface of mirror polished graphite plates with surface area of 0.6×0.6 cm². Preparation stages of ppy/Pt-Cu catalyst were as follows: to 10 ml of 3 mM K₂PtCl₆ + 1 M CuCl₂.6H₂O in distilled water, a solution of 0.1 M NaBH₄ + 1 M NaOH was added drop wise under vigorous agitation. Then, the solution was ultrasonicated for five minutes and mixed with 10 ml of 0.2 M pyrrole + 0.3 g KCl solution. One of the ppy/Pt-Cu catalysts was made by placing a graphite plate in the final solution and cycling the voltage between +0.98 and -0.78 V with scan rate of 5 mV s⁻¹ for 5 cycles. The second catalyst (ppy/Pt-Cu(GS)) was formed from the similar solution via galvanostat method at 70 mA/cm². The solutions were deaerated carefully with Ar before each synthesis.

Electrochemical experiments were performed in form of three-electrode cell at room temperature. The specimens were used as working electrode, platinum as counter electrode and saturated calomel as reference electrode. Electrochemical tests were conducted on EG&G electrochemical system for evaluating the efficiency of the catalysts towards ORR. Solutions of saturated oxygen and deaerated 0.5 M H_2SO_4 were used as electrolyte for electrochemical tests. Scanning electron microscopy (SEM) and Energy-dispersive X-ray spectroscopy (EDS) were used for characterizing the morphology and Pt/Cu ratio of catalyst layers. Cyclic voltammetry measurements were performed in 0.5 M H_2SO_4 at a sweep rate of 20 mV s⁻¹ to calculate electrochemical active surface areas of the catalysts. The metal loading of Pt deposited on ppy support was determined by inductively coupled plasma (ICP).

3. RESULTS

Fig. 1 shows the SEM images of ppy/Pt-Cu in which the homogeneous coverage of the surface and particles size are shown. The particle size in the matrix of ppy is approximately 60 nm.

Fig. 2(a) and 2(b) show the SEM images of ppy/Pt-Cu(GS) layer that was produced by galvanostatic method at 70 mA cm⁻² constant current density. This layer is not homogenous and is more porous compared to ppt/Pt-Cu. The particle size of the catalyst is about 120 nm. EDS analysis of ppy/Pt-Cu and ppy/Pt-Cu(GS) coatings are shown in Fig. 3(a) and 3(b) respectively. The electrochemically active surface (EAS) of ppy/Pt-Cu and ppy/Pt-Cu(GS) catalysts were 35 m² g⁻¹ Pt and 46 m² g⁻¹ Pt respectively calculated according the literature [24,25]. Inductively coupled plasma (ICP) analysis showed the Pt loading of 0.72 mg cm⁻² and 0.68 mg cm⁻² for ppy/Pt-Cu and ppy/Pt-Cu(GS) respectively.



Figure 1. SEM image of (a) ppy/Pt-Cu catalyst with (b) approximate particles size of 60 nm.



Figure 2. SEM image of (a) ppy/Pt-Cu(GS) catalyst with (b) approximate particles size of 120 nm.

Cathodic polarization tests were performed on both catalysts. The results are shown in Fig. 4. More catalytic activity can be observed for ppy/Pt-Cu(GS) indicating higher ORR rate for ppy/Pt-

Cu(GS) catalyst compared to ppy/Pt-Cu catalyst. This can be attributed to the higher contact surface area for this catalyst, which provides higher catalytic sites and therefore higher current densities.



Figure 3. EDS spectra of the (a) ppy/Pt-Cu and (b) ppy/Pt-Cu(GS) catalysts.



Figure 4. Cathodic polarization curves of ppy/Pt-Cu and ppy/Pt-Cu(GS) catalysts in oxygen saturated solution of 0.5 M H_2SO_4 with scan rate of 5 mV s⁻¹.

A peculiar phenomenon that can be observed in this test is a peak around 0.7 V for ppy/Pt-Cu catalyst which may be due to the entrapment of O_2 gas in the pores of ppy layer which was reduced first. As this process finishes, the current reduces and the rest of the current is limited by diffusion of O_2 from the solution to the surface.

Fig. 5 shows the cathodic polarization curves in O₂ saturated and deaerated solutions. After deaerating, the peak around 0.7 V for ppy/Pt-Cu catalyst disappeared. This observation confirms our mentioned hypothesis about the source of this peak. The ppy/Pt-Cu(GS) catalyst is more porous and diffusion of electrolyte to the active areas is faster in this case compared to the ppy/Pt-Cu catalyst. Therefore, the peak is less dominant in polarization curve for ppy/Pt-Cu(GS) and it can be seen as a small peak around 0.5 V. Moreover, it should be noted that in the absence of oxygen in the electrolyte, the current densities are decreased confirming that the current densities observed for ppy/Pt-Cu(GS) and ppy/Pt-Cu(GS).



Figure 5. Cathodic polarization curves of ppy/Pt-Cu and ppy/Pt-Cu(GS) catalysts in oxygen saturated (O₂ sat.) and deaerated (Ar sat.) solutions of 0.5 M H₂SO₄ with scan rate of 5 mV s⁻¹.

To investigate the reaction in forced connection mode, the catalysts were made on rotating disk electrodes. The results of rotating electrode test for ORR can be seen in Fig. 6(a) and 6(b). As can be seen, higher current densities are obtained at higher electrode rotation speeds. This trend also demonstrates the diffusion nature of ORR on these catalysts. Similar to the results of normal polarization tests, the rotating disk electrode tests also suggest that ppy/Pt-Cu(GS) is more active toward ORR than ppy/Pt-Cu catalyst. The number of participated electrons can be estimated from Levich equation: $i_L=0.62nFAC_oD^{2/3}v_k^{-1/6}\omega^{1/2}$ (1)

Where i_L is the limiting current density in $\mu A \text{ cm}^{-2}$, n is number of participated electrons in reaction, A is the electrode area, C_0 is the concentration of dissolved O_2 (1.03×10⁻⁶ mol cm⁻³), D is the

diffusion coefficient of O_2 (2.1×10⁻⁵ cm² s⁻¹), v_k is the kinematic viscosity of the electrolyte solution (1.07×10⁻² cm² s⁻¹), and ω is the rotation rate represented by rad s⁻¹ and F is the Faraday constant (96500 C mol⁻¹) [26].



Figure 6. Rotating disk electrode tests for the (a) ppy/Pt-Cu and (b) ppy/Pt-Cu(GS) catalysts, performed in oxygen saturated solution of 0.5 M H_2SO_4 with scan rate of 5 mV s⁻¹.

Fig. 7 compares the slope of experimental plotted i_{L-1} versus ω^{-1} to the theoretical curves for two and four electron participated reactions. Both of the catalysts show four electron ORR and indicate that H₂O is the final product of ORR.



Figure 7. Levich plots for various catalysts and theoretical lines for two and four participated electron in reaction.

The results of electrochemical impedance are displayed in Fig. 8. As shown in Nyquist diagrams of the catalysts, each catalyst layer has two loops at higher frequencies, related to the reactions on the surface and in porosities, followed by a diffusion line at lower frequencies. Diffusion line is more dominant in the case of ppy/Pt-Cu(GS) because of higher porosity. The results of EIS tests were analyzed using Zview software.



Figure 8. Nyquist plots of ppy/Pt-Cu(GS) and ppy/Pt-Cu catalysts in oxygen saturated solution of 0.5 M H₂SO₄.



Figure 9. Equivalent circuit for modeling the behavior of ppy/Pt-Cu and ppy/Pt-Cu(GS) catalysts in oxygen saturated solution of 0.5 M H₂SO₄.

Fig. 9 shows equivalent circuit for modeling the behavior of the catalysts. As shown in Fig. 9 the equivalent circuit is composed of two time constants in series. In the equivalent circuit Rs represents the resistance of the solution. Rct1 and CPE1 are corresponding to the charge transfer resistance and the double layer capacitance of surface respectively. Rct2 and CPE2 are charge transfer resistance and the double layer capacitance within the porosity. W1 and W2 are Warburg elements which describe diffusion of electrolyte to the catalytic sites. The values of the fitting circuit elements using equivalent circuit of Fig.9 show lower charge transfer resistance for the ppy/Pt-Cu(GS) catalyst (401 Ω cm²) compared to the ppy/Pt-Cu catalyst layer (494 Ω cm²). This can be attributed to the higher porosity and higher EAS value for ppy/Pt-Cu(GS) catalyst layer. Lower Rct value suggests higher ORR rate for ppy/Pt-Cu(GS) catalyst.

4. CONCLUSIONS

(1) The composite ppy/nano Pt-Cu(GS) is a noble catalyst for ORR due to the higher porosity of the catalyst layer and provision of a more active area for the catalysts.

(2) Higher porosity of ppy/nano Pt-Cu(GS) is the key factor for the improved efficiency.

(3) The method of preparation plays an important role in creating the porosity and the size of catalyst particles.

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