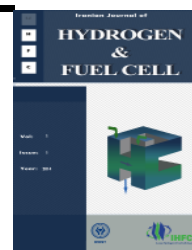


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Oxygen reduction reaction on Pt/C at the presence of super paramagnetic of Fe₃O₄ nanoparticles for PEMFCs

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Abstract

In this paper the role of super paramagnetic iron oxide nanoparticles (SPI) on Platinum nanoclusters on activated carbon (Pt/C) for electrocatalytic oxygen reduction reaction was considered. Four composites of Pt/C and super paramagnetic iron oxide nanoparticles were prepared with the same total composites weight and different loading of Pt/C (1.2, 0.6, 0.4 and 0.3 mg). The composite attached on a glassy carbon electrode via a thin layer of Nafion, that was made by Nafion solution .

The electrochemical tests were carried out by using conventional three electrode system in sulfuric acid electrolyte at room temperature. Cyclic voltammetry, linear sweep voltammetry, rotating disk electrode configuration and chronoamperometry results showed that by decreasing the Pt/C loading, Electroactive surface area and oxygen diffusion coefficient decreased. Also by increasing the Fe₃O₄ nanoparticles in catalyst composite 2-electron pathway for ORR surpass from 4- electron pathway. Our results showed that in electrode with the same ratio of Pt/C and SPI has the best utilization of Pt for oxygen reduction reaction.

1. Introduction

Low temperature fuel cell technology is an important popular technology for transportation purposes. Ion-exchange polymer membrane fuel cell (PEMFC) is an electrical power source that is fed by hydrogen gas and produces water. However, commercialization of this technology is a matter of challenge due to the cost of platinum and its limited sources [1]. There-

fore, research is focused on the potential alternatives to reduce the cost of low temperature fuel cell, which can be produced by two strategies:(a) reduction of platinum loading in the catalyst layer of electrodes, and (b) replacing the platinum catalyst by non- platinum catalysts [1]. The electrochemical reduction of oxygen is one of the most important reactions in electrochemistry due to its central role in the function of metal-air batteries in fuel cells [1, 2].

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According to the catalyst material and the electrolyte composition, the oxygen reduction reaction (ORR) proceeds as a direct four-electron process or a two-electron pathway. The production of water, or four-electron reduction pathway is favorable in PEMFC; while hydrogen peroxide is electrochemically generated by a two-electron reduction of oxygen and causes a decrease in the PEMFC operation voltage. [2].

Some transition metal oxides, such as iron, cobalt, manganese and ruthenium can modify the electronic nature of platinum for ORR and are effective in reduction of the platinum loading in PEMFCs. Also, these transition metal oxides have appropriate activity for oxygen reduction reaction [3, 4].

Fe₃O₄ nanoparticles have some benefits such as low cost and environmental compatibility in comparison to other metal oxides. Recently, much research has been done in this subject. Lai et al. [5] applied platinum nanoparticles on the surface of three-dimensional Fe₃O₄/C particles and used it as a methanol oxidation reaction (MOR) catalyst. The current density of MOR for this catalyst is three times greater than Pt/C.

Oxygen is a paramagnetic molecule and the magnetic field affects its mobility in the catalyst layer of fuel cells. Okada et al. studied the effect of magnetic field on the performance of the ORR in PEMFC. They showed that magnetic field increased the rate of ORR [9]. Zeng et al. investigated the role of magnetically modified Pt composites with Polyaniline fibers for oxygen transport in zinc air fuel cell [10]. Also, some research has been done on the effect of magnetic field on the proton transport or its electro-reduction in porous electrodes [11-13].

Hung et al. used binary catalyst consisting of Pt/C and Fe₃O₄ nanoparticles for methanol oxidation. They observed that adding Fe₃O₄ caused a decrease in CO poisoning of platinum clusters [15].

In this study a physical mixture of commercial Pt/C and super paramagnetic nanoparticles of Fe₃O₄ with four different mass ratios were attached to a glassy carbon electrode; then, the kinetic of ORR in these electrodes were evaluated via a three electrode configuration cell.

2. Experimental

80 mg Pt/C (10 wt.%, fuel cell store) super paramagnetic iron oxide nanoparticles (SPI) that had been prepared by another research group in our

collage [18-19] were added to 20ml distilled water and 2-propanol (with the same ratio). The mixture was dispersed for 30 minutes using the ultrasonic waves. Four inks were prepared by the above procedure with different weights of SPI (80, 160, 240 and 320 mg). The four inks were placed in oven at 80°C for 30 min. Then, 20 μl of ink was applied on a mirror-polished glassy carbon electrode with π cm² area. After evaporation of the solvent, 20 μl Nafion solution (5 wt. %, Ion power) was added to the dried catalyst ink. The electrochemical measurements on electrode were performed with a saturated Ag/AgCl saturated reference electrode and a 0.8 cm² area Pt foil (as counter electrode) in 0.5M sulfuric acid electrolyte. An EG&G PARSAT 2273 Potentiostat/Galvanostat was connected to this three-electrode configuration. All the electrochemical experiments were performed at room temperature. Cyclic voltammograms were recorded in argon atmosphere after 100 cycles with -0.3 - 1.2 V (vs. Ag/AgCl electrode) and 50mVS⁻¹ scan rate. Linear sweep voltammograms were recorded in oxygen atmosphere, with 1-0V (vs. Ag/AgCl electrode) and 1mVS⁻¹ scan rate. For Chronoamperometry measurements, the working electrode potential was kept at 1.2V (vs. Ag/AgCl electrode) for 60 seconds, and then at 0.3V for 10 seconds.

3. Results and discussion

3.1. Cyclic Voltammetry

We obtained Cyclic voltammograms in -0.3 to 1.2V in 0.5M sulfuric acid solution and inert gas purging in solution (figure 1). The electrochemical specific surface areas (EAS) of electrocatalysts were calculated by integrating the areas of hydrogen adsorption peak on Pt using Equation (1)[6]:

$$EAS = \frac{Q_H}{[Pt] * 0.21} \quad (1)$$

In this equation, Q_H is the charge of H adsorption on Pt and [Pt] the loading of Pt in catalyst attached on GC. The results of EAS are presented in Table 1 for different electrodes.

Our results show that the magnetic properties of SPI facilitate the proton transport and adsorption on Pt nanoparticles [Equation (2)]. Tanga et al. demonstrated that magnetic field increases the proton transportation in active layer media [13].

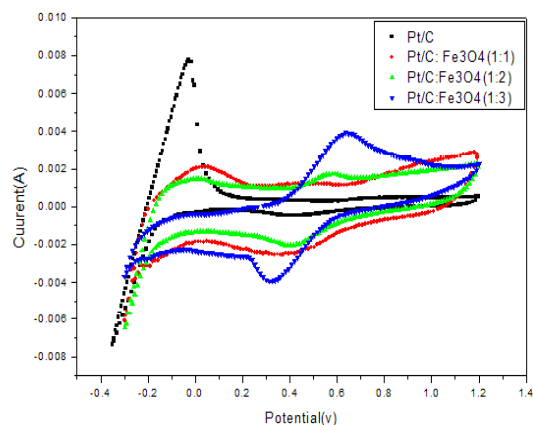
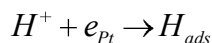


Figure 1. Cyclic Voltammetry of electrodes, with Pt/C: SPI ratio, (1:0, 1:1, 1:2 and 1:3) with the scan rate 50mvs^{-1} and N_2 atmosphere at room temperature and 0.5M sulfuric acid electrolyte at room temperature.

Also, by increasing the SPI content, oxidation/reduction of $\text{Fe}^{2+}/\text{Fe}^{3+}$ pair appeared in cyclic voltammograms [20].

Table 1. Electrochemical active surface area for different electrodes

electrocatalyst	EAS(cm^2g^{-1})
Pt/C	124.90
Pt/C : $\text{Fe}_3\text{O}_4(1:1)$	106.11
Pt/C : $\text{Fe}_3\text{O}_4(1:2)$	61
Pt/C : $\text{Fe}_3\text{O}_4(1:3)$	33.36

3.2. Chronoamperometry

Chronoamperometry technique is an effective method to evaluate the diffusivity, solubility and permeability of oxygen molecule in the electrode media. These parameters can be evaluated according to the Cottrell equation: [7]:

$$i(t) = \frac{nFAD_b^{1/2}C_b}{(\pi t)^{1/2}} \quad (2)$$

where, n is the number of exchanged electrons for the overall electrode electrochemical reaction. A , F , t and π are the area of the electrode, Faraday's constant, the time, and the ratio of circumference to diameter, respectively. D_b and C_b are diffusion coefficient and oxygen concentration, respectively. Figure 2 shows the plot of current vs. t for different electrodes. By The

diffusion coefficient of oxygen for different electrodes is calculated using Cottrell equation and listed in Table 2.

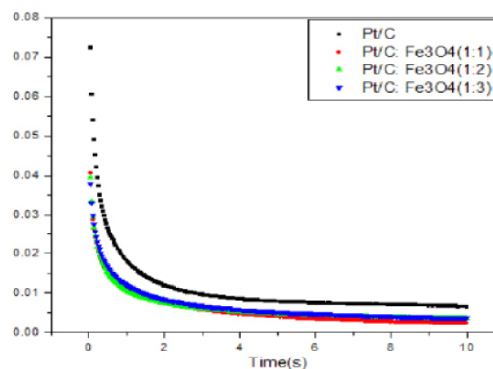


Figure 2. Chronoamperometry plots in O_2 saturated sulfuric acid electrolyte at room temperature.

Table 2. Diffusion Coefficient of Oxygen obtained from Cottrell equation.

electrocatalyst	D_{O_2} (cm^2/s)
Pt/C	1.13×10^{-5}
Pt/C : $\text{Fe}_3\text{O}_4(1:1)$	3.93×10^{-6}
Pt/C : $\text{Fe}_3\text{O}_4(1:2)$	3.18×10^{-6}
Pt/C : $\text{Fe}_3\text{O}_4(1:3)$	3.18×10^{-6}

Chronoamperometry results show that the electrode with 80mg of SPI has a better media for diffusion of oxygen compared to other electrodes. But, in other electrodes, increasing the content of SPI caused the diffusion of oxygen to remain nearly constant.

3.3. Rotating disk electrode (RDE) voltammetry

The ORR activities of electrodes were investigated in O_2 saturated 0.5M H_2SO_4 solution. Figure 3 shows the linear scan voltammetry plots of electrodes measured with a scan rate of 1mvs^{-1} at room temperature with different electrode rotating speeds ranging from 100 to 2000 rpm. To obtain kinetic parameters for the oxygen reduction reaction at fabricated electrodes followed [8]:

$$\frac{1}{i} = \frac{1}{i_k} + \frac{1}{i_d} \quad (3)$$

where i , i_k and i_d are current density, kinetic current density and diffusion limited current density respectively. To investigate the mechanism of

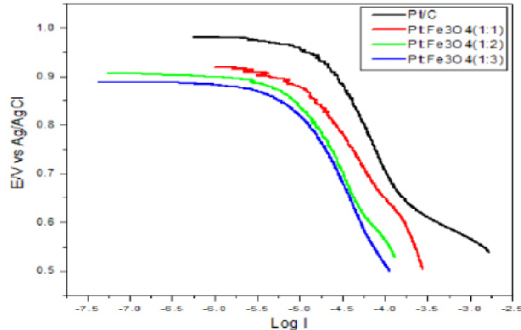


Figure 3. Linear sweep voltammetry on RDE for Pt/C: SPI ratio (1:0, 1:1, 1:2 and 1:3) in H_2SO_4 (0.5M) and scan rate mvs^{-1} from 100 rpm to 2000 rpm at room temperature.

ORR in the electrodes, the Koutecky–Levich [14] plots were prepared and the number of electron transferred in ORR was evaluated (Table 3). The results showed that the mechanism of ORR switches from 4-electron mechanism to 2-electron pathway by increasing the SPI content. Wu et al. [16] and Zho et al. [17] demonstrated the peroxide formation on iron oxide particles during the oxygen reduction reaction. So, by optimization of SPI content, the ORR follows the 4-electron pathway.

Table 3. Number of electrons transferred and low current density region Tafel slope for ORR in different electrodes.

electrocatalyst	Number of electron	Tafel slope ($mVdec^{-1}$)
Pt/C	3.6	-62
Pt/C : Fe_3O_4 (1:1)	2.9	-88
Pt/C : Fe_3O_4 (1:2)	2.4	-75
Pt/C : Fe_3O_4 (1:3)	2.4	-62

Tafel slope for low current density region of polarization curves were obtained and are listed in Table 3. Since like platinum, SPI has catalytic behavior for ORR, the Tafel slope for different combinations of both catalysts is nearly similar.

4. Conclusions

In this study the low loading of Pt (10%wt) was used as the cathode PEMFC for ORR with super paramagnetic of Fe_3O_4 nanoparticles. Our work focused on the decreasing of the loading of Pt without the loss of electrocatalytic perfor-

mance for ORR. As the CV results shows, the electroactive surface area of Pt particles reduces, while SPI particle facilitate the proton and molecular oxygen transport in catalyst layer media. Electrocatalytic behavior and magnetic property of SPI that decrease the ORR overvoltage on Pt, enhance the kinetic parameters of electrodes for ORR. Peroxide pathway for ORR on iron oxide particles is preferred [15-16], but rotating disk electrode polarization results shows that optimized loading of SPI and Pt/C with the same ratio follow the four electron pathway.

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