



Study of Graphite addition on electrochemical activity of platinum on zinc oxide electrocatalyst for oxygen reduction reaction in PEM fuel cell

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Abstract:

A fuel cell is an electrochemical device for production of energy from fuel and oxidant. Platinum is the most commonly used catalyst for PEMFC. Catalysts in PEMFC are commonly supported on conductive and porous materials. Carbon is common support for platinum electrocatalyst. Using other materials as supports is attracted researchers for preparing effective electrocatalysts. The preparation of a Pt /zno electrocatalyst for the oxygen reduction reaction in PEM fuel cells was studied in this work. For preparation of electrocatalysts combined process of impregnation and seeding methods were used. The effect of adding Graphite to electrocatalyst and the electrode performance for oxygen reduction reaction was evaluated by three electrode systems. The linear sweep voltammetry (LSV), cyclic voltammetry and impedance Spectroscopy was used for kinetic study of oxygen reduction reaction. Our results show the nano ZnO can be used as a substrate for preparation of platinum electrocatalyst. Also, adding Graphite to the reaction layer improve the electrode performance for oxygen reduction reaction. The optimized concentration of Graphite in the reaction layer is 50%.

Key words: Oxygen reduction reaction; fuel cell; gas diffusion electrode; electrocatalysts; platinum on zinc oxide , non-carbon substrate

Introduction:

Today, fuel cells are widely considered to be efficient and non-polluting power sources offering much higher energy densities and energy efficiencies compared to other current/conventional systems. A fuel cell is an 'electrochemical' device that converts the chemical energy of a fuel (e.g. hydrogen, methanol, etc.) and an oxidant (air or pure oxygen) in the presence of a catalyst into electricity, heat and water. The main objective in fuel cell technologies is to develop lowcost, high-performance and durable materials. A good interaction between the catalyst and the support not only improves catalyst efficiency and decreases catalyst loss but also governs charge transfer. The support can also assist in sufficiently enhancing the catalyst performance and durability by reducing catalyst poisoning (e.g. CO, S, etc.); and in some cases it affects the catalyst particle size. Hence, the choice of support material is vital and highly influential in determining the behavior, performance, longevity and cost effectiveness of the catalyst and the overall fuel cell. However, a multitude of materials other than CBs have been investigated as catalyst supports for PEMFCs. Over the last decade or so, the focus has shifted towards nanostructured supports as they enable

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faster electron transfer and high electrocatalytic activity. Broadly, these may be classified into two main categories: (i) carbon based/carbonaceous supports and (ii) non-carbonaceous supports. Among non-carbonaceous based materials, Titanium oxide, Silicon dioxide, Tin oxide, Indium tin oxide nanostructures have been investigated. The search for non-carbonaceous based supports is particularly essential to deal with the issue of carbon corrosion, which is suffered by all carbon supports. Corrosion of the support inherently leads to further issues like loss of catalyst, which drastically affects the overall performance of the fuel cell [1-5,8]. Huang et al. prepared titania supported Pt electrocatalyst for PEMFC cathode. Accelerated degradation test (ADT) studies revealed 10-fold higher ORR for Pt/TiO₂ compared to commercial Pt/C (45.9 wt.% TKK). The authors concluded that Pt/TiO₂ was found to be highly durable and stable as cathode catalyst for PEMFC [6]. Studies conducted by Matsui et al. revealed that when SnO₂ supported Pt catalysts were heat-treated at various temperatures under oxidizing or reducing atmospheres, their catalytic activity for electrochemical oxidation of CO were enhanced because of their peculiar microstructure and metal-support interactions [7].

In this study among different transition metals, the use of ZnO as a substrate has attracted interest because Zinc oxide is one of the most important semiconductor material with direct band gap (3.37 eV or 375nm), good transparency and high electron mobility (>100 cm²/v.s). It has attracted increasing attention due to excellent electrical properties, inexpensiveness, relative abundance, chemical stability towards air. Since ZnO is an important trace element for humans, it is environment friendly and suitable for in vivo application. So we study of Graphite addition on electrochemical activity of platinum on zinc oxide electrocatalyst for oxygen reduction reaction in PEM fuel cell.

Experimental section:

Synthesis nano ZnO powder:

First, 1.0 mmol Zn(CH₃COO)₂·2H₂O was poured in an agate mortar. Then, 4 mmol NaOH was added to the sample and ground for 60 min at room temperature. Finally, the white mixture was transferred to a beaker and washed fully with distilled water and ethanol for several times and dried at room temperature [9].

Electrocatalyst preparation:

Initially, the Pt solution was obtained by H₂PtCl₆ (Fluka) and then adjusting the solution pH with 1 M NaOH, as required, to the desired value. The Zinc oxide slurry was prepared by dispersing of Zinc oxide in de-ionized water, sonicating for 10 min. For the seeded electrocatalyst was prepared by mixing approximately 10% (v/v) of the Pt solution with the Zinc oxide slurry and sonicated for 30 min. The seeded powder was obtained by the reduction of the previous solution with 0.1 M NaBH₄, sedimented by centrifugation and the pellet was harvested and dried by oven. Thereafter, the obtained powder, covered by the seeded Pt, was dispersed in de-ionized water, sonicated for 30 min and then added to the remaining Pt solution (90%) to the required metal loading on Zinc oxide substrate (12.0–35.8% (w/w)). The mixture was again reduced with 0.1 M NaBH₄ under sonication to obtain the catalyst powder, which settled from the solution. The electrocatalyst solution was filtered, washed thoroughly with de-ionized water and dried overnight at 110 °C [10].



Preparation of electrodes:

For the electrode, the catalyst ink was obtained from mixing 1.0 ml of 2-propanol, 1ml distilled H₂O with 30 wt.% of polytetrafluoroethylene solution and 3 mg of electrocatalyst, sonicating them at room temperature for 30 min to obtain the ink which was then coated onto a carbon paper and dried at 200°C for 60 min. This electrode is labeled Pt/zno. Other electrodes are fabricated at various content of Graphite [10].

Electrochemical analysis:

All the electrochemical measurements were carried out using a potentiostat at 27°C in a three electrode system. All the electrode potentials in this work are related to the reference Ag/AgCl electrode in a 0.5 M H₂SO₄ aqueous solution electrolyte. The working electrode was amount of synthesized electrocatalyst powder was coated on Carbon paper and Pt electrode as a counter electrode was used. Linear sweep voltamograms (lsv) were recorded from 0.8 to -0.2 V vs Ag/AgCl in oxygen saturated electrolyte. Cyclic voltammetry technique (CV) in nitrogen saturated electrolyte was performed to calculating the electrode surface area from 0.8 to -0.2 V at 50 mVs⁻¹ scan rate. The electrochemical active surface area (ECAS) is an important parameter in the characterization of Pt electrocatalysts. The ECAS was determined from CV data in the hydrogen adsorption-desorption region using EQ (1). L_{Pt} loading of Pt

$$ECSA(m^2 / g Pt) = \frac{Q_H}{L_{Pt} Q_F} \times 10^{-4} \quad \text{and } Q_F \text{ is } 0.21 \text{mc.}$$

(1)

Impedance spectroscopy is an electrochemical technique with broad applications that is growing in importance. Measurement of current and potential under a steady state yields some information concerning a given system. By adding frequency dependence to the macroscopic measurements, impedance spectroscopy expands the information that can be extracted from the measurements. Impedance measurements, however, are not sufficient. Additional observations are needed to gain confidence in the model identification. This technique was used and Nyquist plots were recorded at 10 mHz to 100 KHz frequency.

Results and discussion:

Linear sweep voltamograms (lsv) were obtained under O₂ at 27°C, at a scan rate of 1 mV/s in a 0.5 M H₂SO₄ solution from 0.8 to -0.2 V vs Ag/AgCl. The lsv of fabricated electrodes are shown in the Figure 1, as it was seen the ORR current is increasing with decreasing the potential for all of them. By adding Graphite to the electrodes, the performance of electrodes is improved. So that in 50% Graphite in reaction layer of electrodes, the maximum current density was obtained.

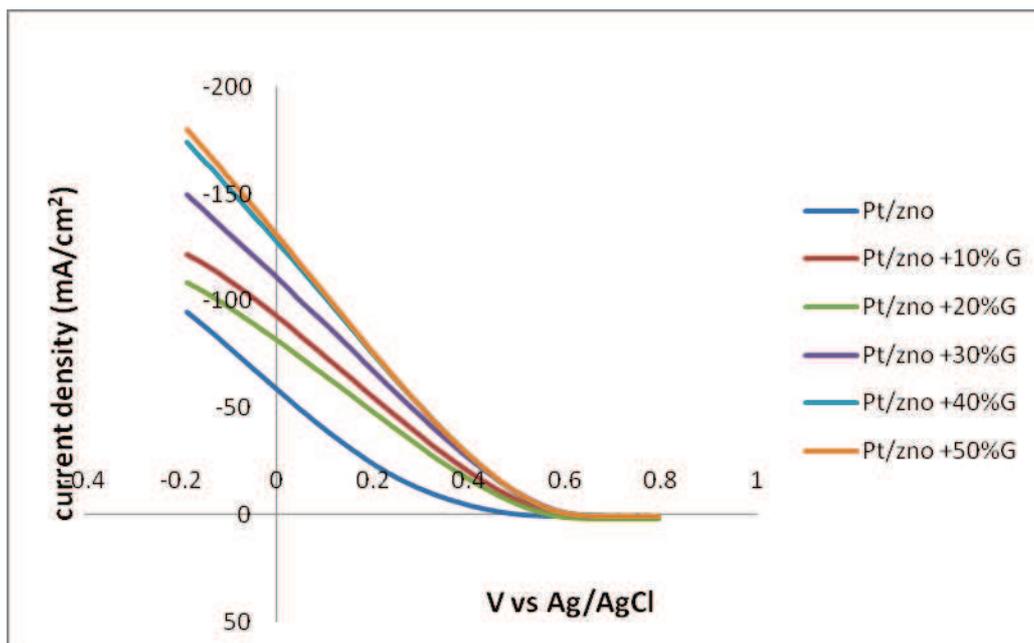


Figure1: polarization plot of 6 electrodes under O₂ at 27°C, at a scan rate of 1 mV/s in a 0.5 M H₂SO₄ solution from 0.8 to -0.2 V vs Ag/AgCl

Figure.2 is shown the Nyquist plots of fabricated electrodes for ORR. According to these results, the best performance of fabricated electrodes for ORR is observed in 50% Graphite in reaction layer.

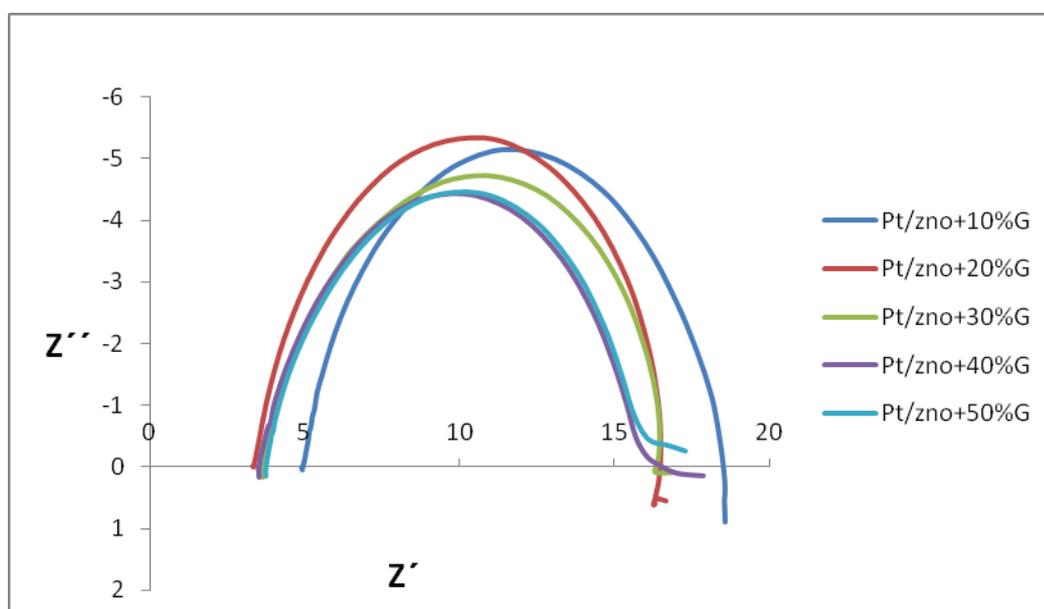


Figure 2: Nyquist plot of 5 electrodes under oxygen at 27°C at 0.5V in a 0.5 M H₂SO₄ solution

The electrochemical surface area of electrodes can be achieved by cyclic voltammetry technique (figure.3). It can be realized the maximum surface area is belonged to 50% Graphite in electrode.

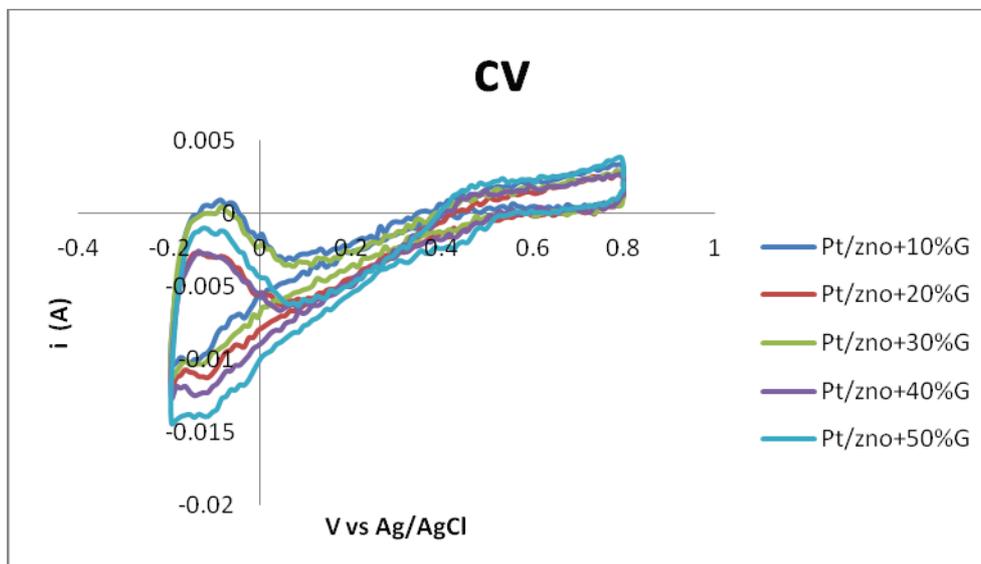


Figure3: cyclic voltammograms of electrodes in H₂SO₄ 0.5 M electrolyte at 50 mV/s and 27°C

Conclusion:

Electrocatalyst substrates play a vital role in ascertaining the performance, durability and cost of PEMFC systems. Pt/zno electrocatalyst was prepared by a combined process of impregnation and seeding methods and prepared electrocatalyst showed an enhancement of electrocatalytic activity toward the ORR process in acid medium. The electronic changes are related to an apparent strong interaction of Pt centers with zinc oxide. On the other hand, in this work adding Graphite to Pt/zno electrocatalyst was studied, according our results, adding Graphite to the reaction layer of fabricated electrodes can improve performance of electrode and increase ORR current and exchange current density. The optimized concentration was found in 50% Graphite in the reaction layer.

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