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The study of synergism effect in physical mixture of Cobalt and platinum electro catalyst for oxygen reduction reaction in PEM fuel cell

Rasol Abdullah Mirzaie*[1], Mohammad safi Rahmanifar[2], Samane Sajedinia[1]
1- Fuel cell Research Laboratory, Dep. Of chemistry, Faculty of science, Shahid Rajaee Teacher Training University, Tehran, IRAN
Corresponding Author E-mail: ra.mirzaei@srttu.edu

Abstract

Gas diffusion electrodes are one of the important parts in fuel cells. Optimizing electrocatalyst is one of the approaches for increasing the efficiency of the electrodes. The aim of the present research project is to increase the catalytic activity toward oxygen reduction reaction (ORR). Hence In this work, Platinum-Cobalt electrocatalyst on Graphite(Pt-Co/G) electrode was prepared by physical mixture of platinum and cobalt electro catalysts. For this purpose, Cobalt on Graphite(Co/G) and Platinum on graphite(Pt/G) mixtures at various percent (20:80, 40:60, 50:50, 60:40, and 80:20) were used for fabrication of gas diffusion electrode in cathode of PEM fuel cell. The amount of electrocatyst in reaction layer was 0.3 mg/cm^2. the metal percentage in prepared electrocatalyst was 20 %. The electro catalytic performance of the electrode was investigated by electrochemical Impedance Spectroscopy (EIS) and Linear Sweep Voltammetry (LSV). according to the results, in the optimized condition the mixture of 80% Pt/G and 20% Co/G electrocatalyst in reaction layer provide excellent electrochemical condition for ORR and promote sluggish ORR compare to other electrodes results from other percent of physical mixture of Pt/G and Co/G electrocatalyst.

Keywords: fuel cell, synergism, Oxygen reduction reaction, physical mixture

Introduction

In the future, technology advances will require that mankind increase their electricity consumption. Fuel cells promise to be a clean power source for the energy requirement of the mankind in the near future. The advantage is an efficient and clean energy production because the waste product is water[1]. Fuel cells can produce electricity continuously as long as the fuel and oxidant flow are maintained. The fuel cells challenge is to find the suitable materials to

achieve this, due to efficiency losses occurring with time by degradation of their components (e.g. catalysts).The high cost of electrode is distributed to the presence of electrocatalyst usually Pt on electrode layer because Pt possesses a high exchange current density for oxygen reduction, a high resistance to chemical attack, excellent high-temperature

1. *Fuel cell Research Laboratory, Dep. Of chemistry, Faculty of science, Shahid Rajaee Teacher Training University, Tehran, IRAN*
2 . *Dep. Of chemistry, Faculty of basic science, Shahed University, Tehran, IRAN*

characteristic, and has stable electrical properties, However, platinum is very expensive and much work has been focused on the reduction of platinum loading and the improvement of electro catalytic activity of platinum [2,3]. possibly, the most significant barrier that proton exchange membrane fuel cell (PEMFC) had to overcome was the costly amount of platinum required as a catalyst[4]. Many studies have reported synergistic properties for mixed systems such as mixed surfactants, physical mixture of catalyst, etc.[5]. In this work, the combined processes of impregnation and seeding was used to prepared Pt–Co/G electro catalysts. The prepared electro catalysts were in physical mixture of Pt and Co electro catalysts for the oxygen reduction reaction in PEM fuel cells.

Experimental

Electro catalyst preparation

Initially, the Pt solution was obtained from metal precursors, H_2PtCl_6 (Merck),in order to reach metal loading of 20%(w/w). The Graphite slurry was prepared by dispersing required amount of graphite 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 graphite slurry and sonicated for 30 min. The seeded powder was obtained by the reduction of the previous solution with 0.1 M $NaBH_4$, sedimented by centrifugation and the pellet was harvested and dried at 110^o C. Thereafter, the obtained graphite 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 graphite substrate (20% (w/w)). The mixture was again reduced with 0.1 M $NaBH_4$ 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^o C. the Co catalyst was prepared in a same process like Pt catalyst, in this case the metal precursor was CoCl2(Merck)[2].

treatment of carbon support

a Carbon paper was used as a gas diffusion layer for fabricating gas diffusion electrode which was a circle with the diameter of 11 mm. in order to remove fat and redundant, carbon paper was rinsed in de ionized water and acetic acid with equal ratio and the dried at 200C.

Preparation of electrode

Pt/G and Co/G electrocatalysts were used for fabricating GDE with the loading of 0.3 mg/cm^2 at various percentage of them (20:80, 40:60, 50:50, 60:40, and 80:20(%w/w)) were used. (in a table 1. Different percent of fabricated electrodes with short names were taken).They mixed to distilled H_2O and C_3H_7OH with equal volumic ratio, then certain amount of polytetrafluoro ethylene (60%wt PTFE, Aldrich) with the loading of 30%, was added and sonicating at room temperature for 30 min, After evaporating the solvents, an uniform paste obtained which uniformly spread over the carbon paper and next sintered at 200 °C for 1 h.

No	percent of fabricated electrode	short name
1	Pt 20%-Co 80% /G	PtCo(28)
2	Pt 40%-Co 60% /G	PtCo(46)
3	Pt 50%-Co 50% /G	PtCo(55)
4	Pt 60%-Co 40% /G	PtCo(64)
5	Pt 80%-Co 20% /G	PtCo(82)

Electrochemical analysis

The oxygen reduction reaction (ORR) was evaluated in the cathode via an approach, in which the current density measured with respect to potential using a half-cell measurement apparatus which comprised a three-electrode system. An Ag/AgCl electrode was employed as the reference electrode, a Pt electrode constructed from Pt plate was utilized as the counter electrode and the GDE described above was used as the working electrode. The GDE was set in a holder and then placed in sulfuric acid (0.5 M). oxygen was introduced into the holder under a pressure of 1 atm. The room temperature was (300 K). The scanning rate, used in the experiments were as 1 $mV.s^{-1}$. The voltage scanned from -0.2 to 0.8 V vs. an Ag/AgCl electrode. by the means of LSV and EIS analysis, synergism effect was studied and the electrode with the highest performance to ORR determined.

Results and discussion

in fig.1The polarization curves for different percentage of physical mixture of platinum and cobalt electrocatalyst were shown. As it was seen, the ORR current was increase with decreasing the potential. the PtCo(82) electrode has highest performance toward ORR compare to others and Platinum electrode either, it means cobalt improve the catalytic activity of platinum electrode. So it could be said that synergism effect was seen in PtCo(82). in Fig. 2 the Nyquist plots of the electrodes were shown. all of them indicate two incomplete semi-circle that overlap each other, by the means of z-view software, equivalent circuit elements were drawn. Since, the diameter of the semi-circle is equal to the polarization resistance, so with decreasing the polarization resistance ORR activity was improved. In the PtCo(82) fabricated GDE, the best performance for ORR was seen. In this electrode, the charge transfer resistance was minimum. It intends to fast electron transfer in the GDE for leading to highest performance for ORR. Also the amount of cobalt in the reaction layer affected on electrochemical activity of electrode for ORR. Except in optimized percent, With increasing of Cobalt amount in reaction layer, the performance of electrode was decreased.

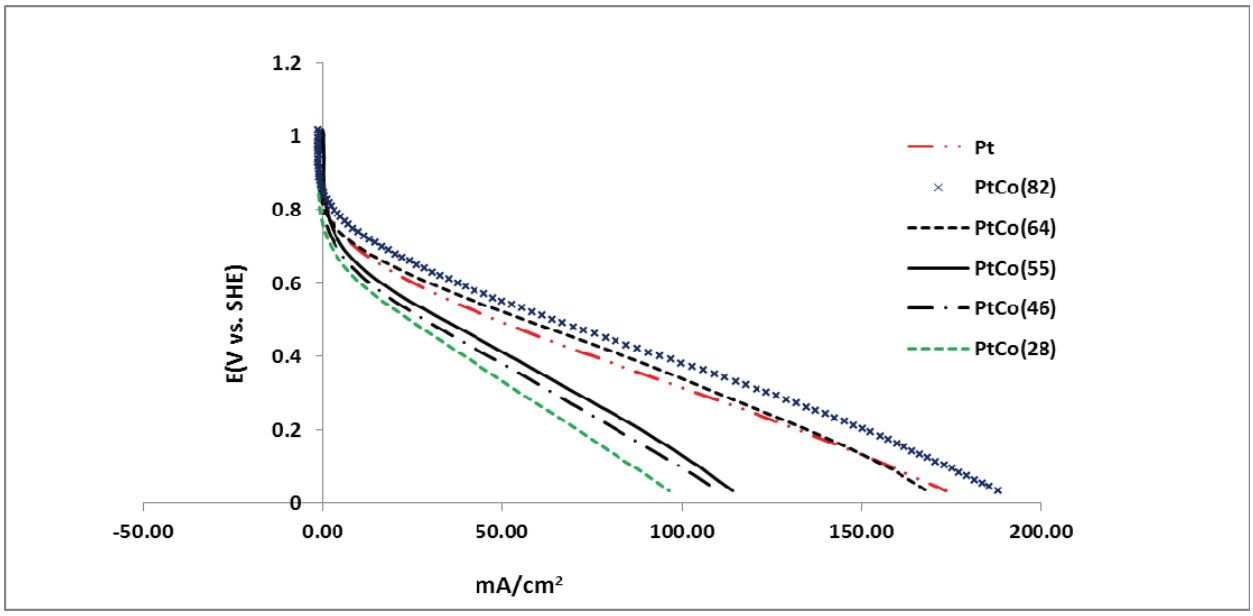

Fig.1. Polarization curves of a single PEM fuel cell for oxygen reduction at potential range of -0.02 to 1 vs. an Ag/AgCl with an electrocatalyst loading on GDL of 0.5 mg/cm^2 when using Pt–Co/G electrocatalyst prepared at metal loading on Graphite substrate of 20% at 300K.

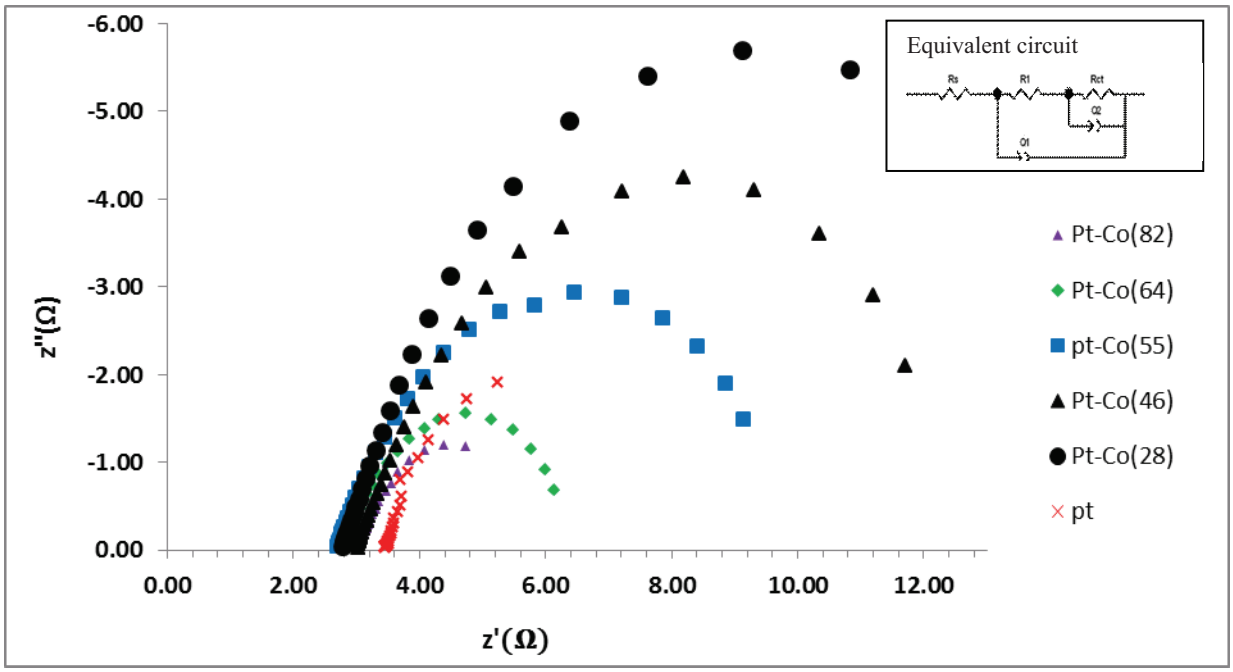

Fig.2. Niquist plots obtain from synthesized electrocatalyst at the potential of 300 mv in frequency range of 15kHz to 10Hz

Conclusion:

In this work, synergism effect in physical mixture of GDEs electrode were studied. According to linear seep voltammetry and impedance spectroscopy, PtCo(82)/G electrode showed synergism effect and had high catalytic activity toward ORR. In other word the presence of Cobalt with percent of 20 % (w/w) in the mixture of Platinum and Cobalt electro catalysts, provide special condition for synergism effect. However in other percent, With

increasing the Cobalt amount in the reaction layer, the performance of electrode was diminished.

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