



Evaluation of the electrocatalytic performance of PtCo/C nanoparticles in different proportions of cobalt for oxygen reduction reaction

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Abstract

Bimetallic nanoparticles with extremely uniform dispersion on conductive-carbon supports are very much needed to improve the kinetics of sluggish electrochemical reactions relevant to fuel cell applications. In this research, bimetallic platinum-cobalt with 20% by weight of platinum on Vulcan carbon was synthesized with different proportions of cobalt to investigate the oxygen reduction reaction. Cobalt to platinum ratios of 1:2, 1:0.33, and 1:3 were prepared using the saturation-regeneration method. The catalytic properties of the catalyst for the oxygen reduction reaction were studied using the electrochemical methods of cyclic voltammetry, chronoamperometry, linear potential scanning voltammetry, rotating disk electrode, and electrochemical impedance spectroscopy. The electrocatalyst made with a ratio of 1:2 PtCo/C exhibited higher ORR activity than the other catalysts tested. In addition, the number of electrons in the oxygen reduction reaction was also calculated, which followed the four electron path for a ratio of 1:2. The physicochemical results (scanning microscope spectroscopy (SEM)) showed a more suitable distribution and better active surface for the 1:2 PtCo/C catalyst, which enhanced the utility of the catalyst for ORR.

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1. Introduction

Massive energy consumption and declining fossil fuels with consequent serious environmental and climate problems are severe threats to a sustainable human society. Developing efficient conversion and storage technologies to fully utilize sustainable and clean energy could be a solution for these issues and is a viable option to reduce dependence on fossil fuels and upgrade the industrial transformation [1-2]. Proton exchange membrane fuel cells (PEMFC) have received considerable attention as promising devices for portable and transport applications due to their high energy density, relatively low operating temperature, and minimal corrosion problems [3-5]. Improving the kinetics of electrochemical reactions, especially the sluggish cathodic oxygen reduction reaction (ORR), is crucial to improving the efficiency of fuel cell-based energy devices. It was reported that the energy consumption associated with ORR is about four times the magnitude of the anodic electrochemical hydrogen oxidation reaction (HOR) and the methanol oxidation reaction (MOR) [6]. Platinum (Pt) is a critical element in making electrocatalysts for oxygen reduction reaction (ORR), which occurs at the cathode of polymer electrolyte membrane fuel cells (PEMFCs) [7-10]. Pt particle agglomeration leads to a reduction in the electrocatalyst surface area and a consecutive decrease in the catalytic activity. Various binary and ternary Pt-based alloy nanoparticles on high surface area supports have been studied to obtain higher Pt mass activity [11-13]. One strategy to enhance the ORR activity and decrease the noble metal loading is to alloy Pt with another transition metal M (e.g., Fe, Co, Ni, Cu, and Mo) [14-19]. Accordingly, many researchers have explored low-platinum-containing bimetallics as well as ternary catalysts. For example, Li et al. have provided a three-step electrodeposition strategy for fabricating binary PtNi and PtCo and ternary PtNiCo alloys as ORR electrocatalysts [20].

Huang et al. designed a custom-structured nanocatalyst (PtCo@Gnp) to encapsulate PtCo NPs with graphene nanopockets (Gnp), which exhibited good electrochemical accessibility and durability under a low platinum group metal loading of 0.070 mgPGM cm^{-2} by employing Pd-Ni/C and Fe-Ni-Co/C catalysts in the anode and cathode sides of the DGFC, respectively [21]. They produced a maximum power density (MPD) of 38 mW cm^{-2} at room temperature. Mohammad Zhiani et al. [22] used a ternary alloy of non-noble metals (Fe, Ni, and Co) for the first time as the anode electro-catalyst for the glucose oxidation reaction in an alkaline half-cell and DGFC. They investigated the electro-catalytic activity of Fe-Ni-Co/C and Pd/C in the half-cell using cyclic voltammetry (CV) and chronoamperometry (CA) techniques. Then, anode electrodes were made by Fe-Ni-Co/C and Pd/C electro-catalysts successfully employed in alkaline passive air-breathing DGFCs. Polarization curves and EIS response of DGFC equipped with Fe-Ni-Co/C were evaluated and compared with DGFC containing Pd/C as an anode electrocatalyst [22]. In this research, in order to increase the surface-to-volume ratio of platinum and their nucleation and to make the size of platinum particles smaller, cobalt-to-platinum ratios of 1:2, 0.33, 1:3 were used to evaluate the oxygen reduction reaction. Reducing the particle size was not necessarily expected to lead to an increase in platinum productivity. Therefore, the above ratios were evaluated and investigated.

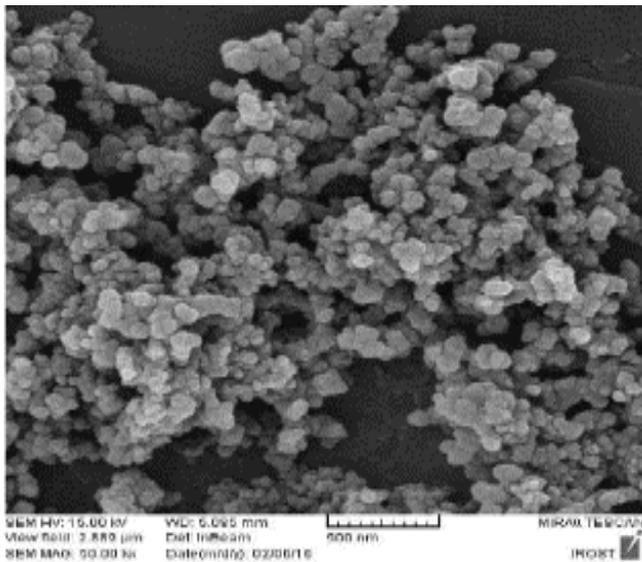
2. Experimental

First, 0.2 g of Vulcan carbon pre-modified with nitric acid, 0.21 g of trisodium citrate, and 0.045 g of Co $(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ salt were added to 80 ml of water and ethanol, then homogenized for 30 minutes in an ultrasonic device. Then, 18.56 ml of NaBH_4 solution and 0.02 M were added drop by drop over two hours.

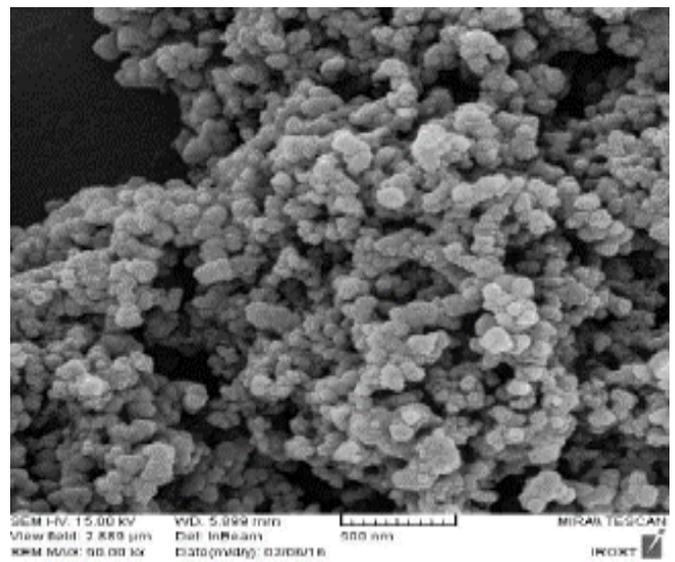
The solution was added while stirring and stirred for another 10 hours. After that, 1.24 ml of 0.001M $H_2PtCl_6 \cdot 6H_2O$ salt was added drop by drop to the solution. After filtering and washing several times with water and ethanol, the sediment obtained was dried for 24 hours in a desiccator under vacuum [23].

3. Results and discussion

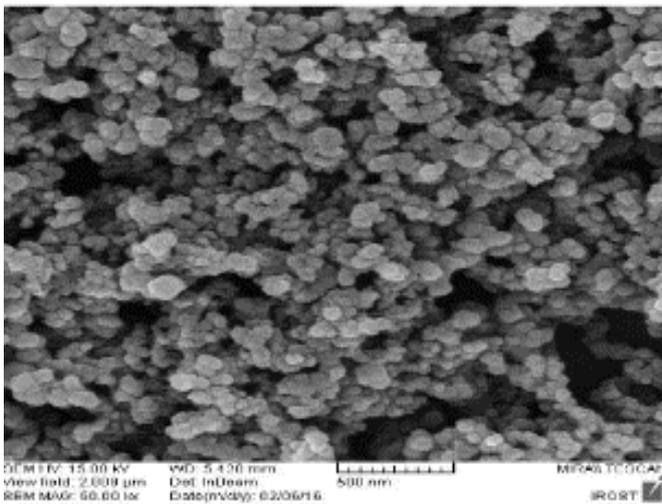
Figure 1 shows the SEM image of the platinum nanoparticles on carbon black powder with different proportions of cobalt and Co/C electrocatalyst. It can be seen that the Pt nanoparticles with a diameter of about 500 nm are distributed almost homogeneously.



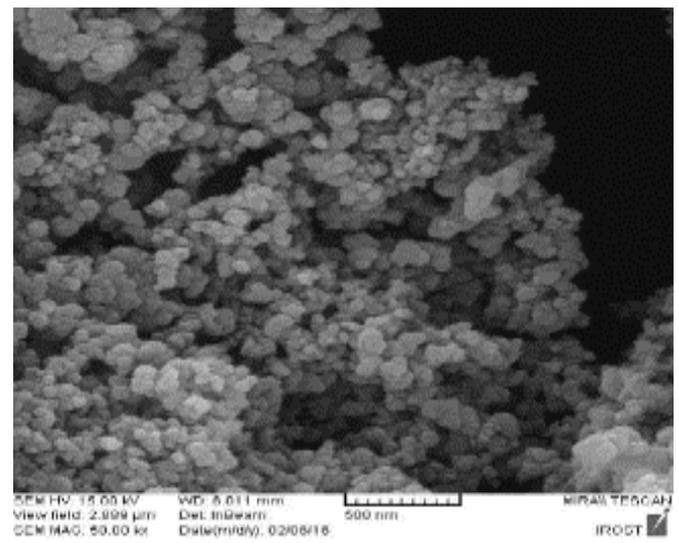
PtCo/C 1:2



PtCo/C 1:3



PtCo/C 1:0.33



Co/C

Fig. 1. SEM images of PtCo nanoparticles supported on carbon black powder with different proportions of cobalt and Co/C electrocatalyst.

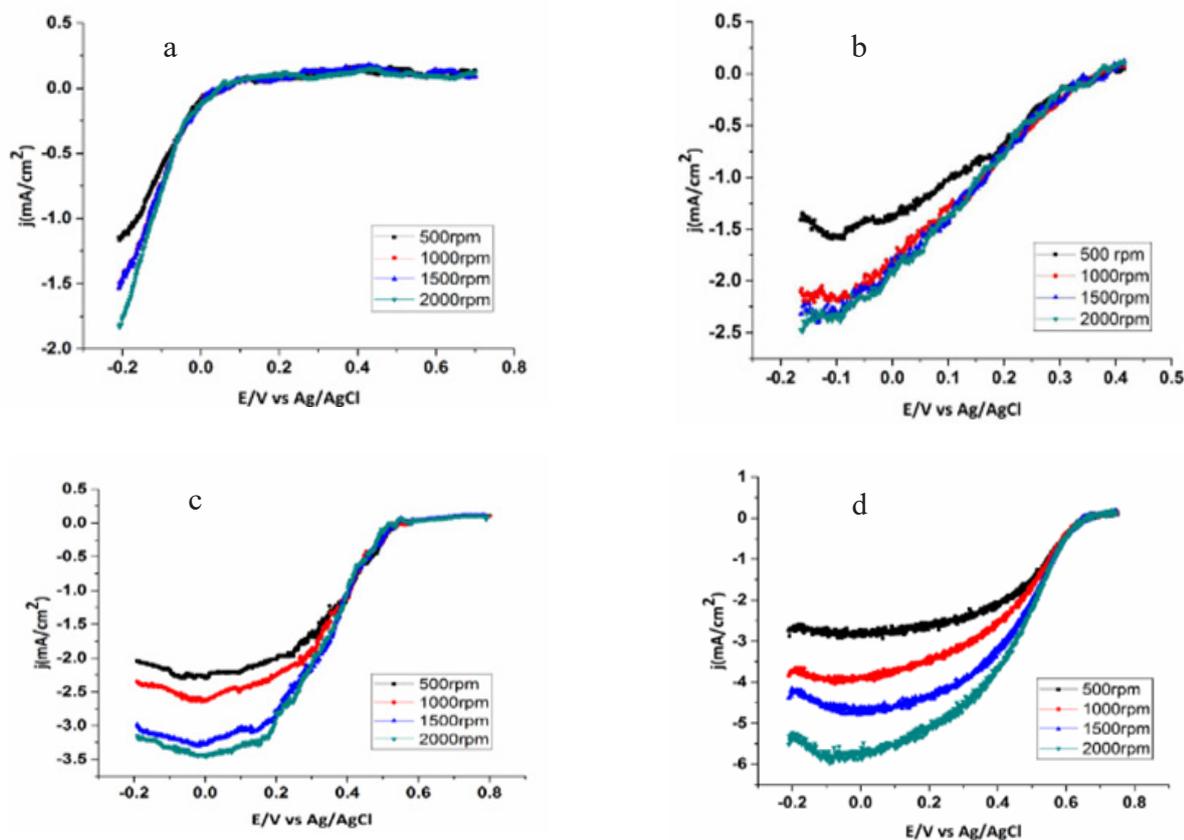


Fig. 2. Oxygen reduction voltammograms for Co/C electrocatalyst and PtCo/C electrocatalyst with different cobalt ratios.

The RDE voltammetric results for the Co/C electrocatalyst in Figure 2a show that the limiting current had little dependence on the change in rotation speed and penetration, and the speed increase from 500 rpm to 2000 rpm decreased the rotation speed and penetration from -1.14 to -1.82 mA/cm². Figure 2b shows the PtCo/C electrocatalyst with a ratio of 1:0.33 cobalt to platinum. As can be seen, the limiting current density at the speed of 500 to 2000 rpm increased from -1.41 to -2.47 mA/cm², but from 1000 to 2000 rpm, the flow changes with penetration decreased. The RDE voltammetry results for the PtCo/C electrocatalyst with a ratio of 1:3 cobalt to platinum shown in Figure 2c show that the limiting current increased from -2.04 to -3.15 mA/cm² at the speed of 500 rpm to 2000 rpm. The RDE voltammetric results for the PtCo/C electrocatalyst with 1:2 ratio of cobalt to platinum shown in Figure 2d show that the limiting current increased

from -2.74 to -5.51 mA/cm² at the speed of 500 to 2000 rpm.

Table 1. Voltammetry with Rotating Disk Electrode

Electrocatalyst	$-J(\text{mA}/\text{cm}^2)(\text{mg}_{\text{Pt}}, \text{cm}^{-2})^{-1}$
PtCo/C 1:2	6.41
PtCo/C 1:3	3.66
PtCo/C 1:0.33	2.87
Co/C	2.12

According to the results obtained from RDE voltammetry, the PtCo/C electrocatalyst with a ratio of 1:2 showed the highest limiting current density.

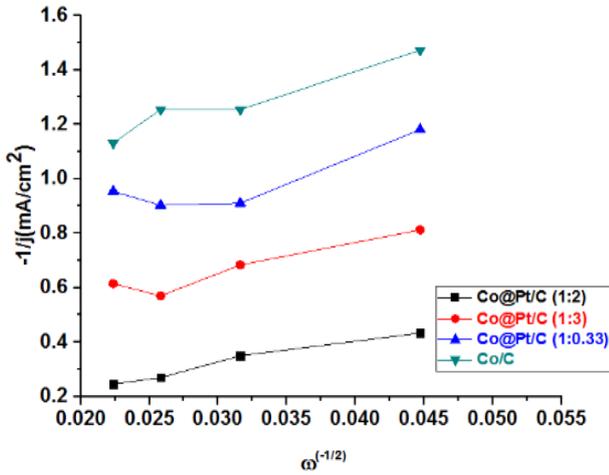


Fig. 3. Kottky-Levich curves obtained from the voltammetry results on the rotating disk electrode in 0.5 M sulfuric acid and oxygen atmosphere at ambient temperature.

To investigate the kinetics of the oxygen reduction reaction and obtain the number of electrons of the exchanged reaction, the RDE results were drawn as a $1/j$ diagram in terms of $\omega^{-1/2}$. According to the RDE voltammetric results, the amount of exchanged electrons during the oxygen reduction reaction for the Pt-Co/C electrocatalyst with a ratio of 1:2 is 3.45, so the mechanism has proceeded through the four-electron

pathway. The number of electrons in the PtCo/C (1:3) electrocatalyst is 2.88. The oxygen reduction reaction has proceeded from both 4-electron and 2-electron paths; that is, there is a parallel path from both paths. For the PtCo/C (1:0.33) electrocatalyst, the electron value is 2.56, which indicates a parallel reaction path. The value of the exchanged electron for the Co/C electrocatalyst was 2.11, indicating that the reaction proceeded through the two-electron pathway.

Table 2. Results of the Kottky-Levich Analysis

Electrocatalyst	The number of electrons exchanged in oxygen reduction (per oxygen molecule)
PtCo/C 1:2	3.45
PtCo/C 1:3	2.88
PtCo/C 1:0.33	2.56
Co/C	2.11

The number of electrons obtained from the slope of the Kottky-Levich diagram is given in Table 2.

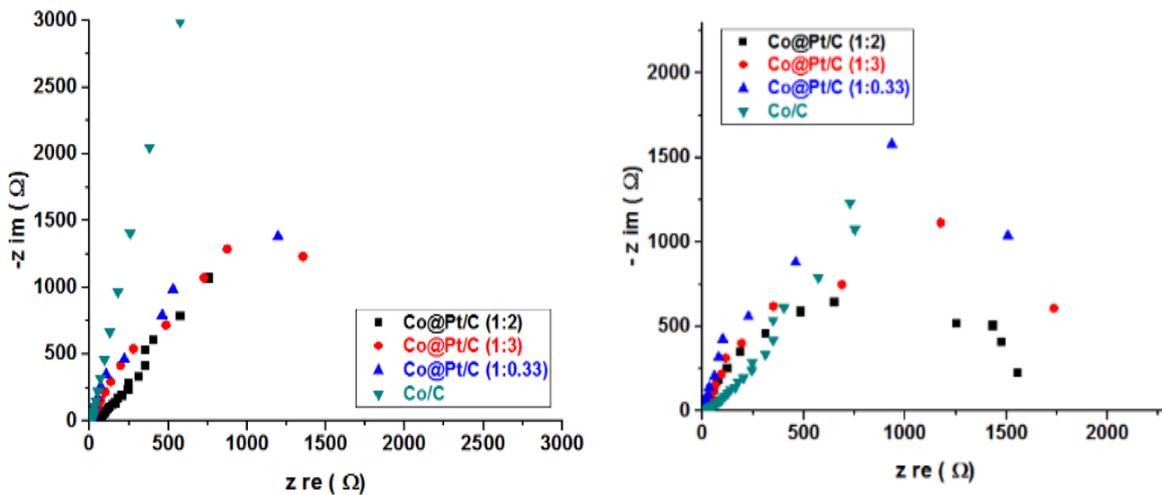


Fig. 4. Comparison of Nyquist curves of different electrodes, at 0 and 0.2 V voltages for oxygen reduction reaction.

According to Figure 4, as the diameter of the semi-circle of the PtCo/C electrode with a ratio of 1:2 to the Co/C electrode increases, the charge transfer resistance decreases. The electrode with a ratio of 1:2 showed the lowest load transfer resistance at this voltage.

Conclusion

To achieve higher particle density, lower resistance, and less use of electrocatalyst for the oxygen reduction reaction in an acidic environment, this study investigated a bimetallic structure of platinum using an inexpensive bimetal as the core for oxygen reduction reaction in an acidic environment. In the synthesis of platinum nanoparticles, the effect of the amount of metal used (cobalt) was taken into consideration. Considering that cobalt metal in tin also plays the role of a weak reducer, the possibility of synthesizing smaller-sized platinum nanoparticles was far from expected. The results of the voltammetry test with the rotating disk electrode also indicated that the current density increases with the increasing speed of the electrode rotation. The results of the Hotkey-Lewich analysis showed that the number of exchanged electrons for the electrocatalyst with a ratio of 1:2 had the highest value, and according to the lower charge transfer resistance obtained from the impedance results, it can be deduced that the electrocatalyst synthesized with a ratio of 1:2 Cobalt to platinum was the most effective and showed the highest electrocatalytic activity.

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