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Synthesis of ^{57}Fe@Pt/C electrocatalysts for active oxygen reduction reaction using E-beam irradiation

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1. Introduction

Recently, research on renewable energy sources has been actively underway due to climate problems and environmental pollution. Among them, research on polymer electrolyte membrane fuel cells (PEMFCs) used in fuel cell electric vehicles and household/building fuel cells is being conducted in various ways. PEMFCs are constituted of an electrode layer in which carbon supports are placed on both sides around a polymer electrolyte film, and a catalyst is dispersed thereon. Catalyst research is also actively conducted because the performance of PEMFCs is affected by the spread and stability of catalysts. Previously, platinum with high catalyst activity was used as the material, but since it is an expensive material, it is necessary to develop an alternative catalyst.

The research direction of platinum-alternative catalysts can be divided into two parts. First, platinum is synthesized with other non-precious metals to reduce the amount of platinum used, and secondly, platinum-free catalysts are developed. In this study, a method for forming a core-shell by combining platinum and iron (^{57}Fe) using electron beam irradiation was selected. Although various methods of synthesis existed in the past, the core-shell can be formed quickly and easily using electron beam irradiation. In the synthesized catalyst, the ratio of Fe and Pt was 2:1 and 1.5:1, respectively, and the results of the synthesis were compared. The shape and electrochemical characteristics of the catalyst synthesized using TEM, XRD, ICP, and CV were confirmed, and the results showed that the ^{57}Fe$_{1.5}$@Pt$_1$/C catalysts were better synthesized.

2. Methods and Results

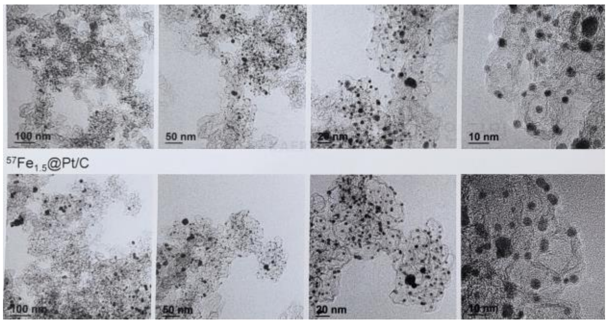
2.1 Catalysts synthesis with E-beam irradiation

^{57}FeCl$_2$ is manufactured to synthesize an iron-based catalyst utilizing a stable isotope ^{57}Fe. In the case of ultrasonic synthesis, only the precursor of ACAC(Acetylacetonate) form shall be used to manufacture the catalyst, but in the case of E-beam irradiation, the precursor of chloride form may also be used. ^{57}Fe of ISOFLEX 96.18 (1 M, 57 g) and HCl (1 M, 36 g) is used to make ^{57}Fe metal into chloride. First, 100 mg of ^{57}Fe is dissolved in about 10 ml of HCl. After removing non-melting metals using a magnet bar, ^{57}Fe-dissolved HCl solution was boiled, then ^{57}Fe-chloride was left. ^{57}FeCl$_2$ in ethanol was prepared by injecting 10 ml of anhydrous ethanol.

Consequently, the ^{57}Fe@Pt/C catalysts are synthesized by using the manufactured ^{57}FeCl$_2$. After combining ^{57}Fe$_{1.5}$@Pt$_1$/C and ^{57}Fe$_2$@Pt$_1$/C, the ratio of Fe and Pt was 1.5:1 and 2:1, respectively, and the efficiency was compared. The synthesis process was based on the synthesis process of 00. Materials used for the synthesis are ^{57}FeCl$_2$ in ethanol, ethylene glycol ($C_2H_6O_2$, F.W=62.07), polyvinylpyrrolidone (PVP), platinum chloride ($PtCl_4$, F.W=336.9), and KB-600J. First, ^{57}Fe$_2$@Pt$_1$/C is manufactured. Mix ^{57}FeCl$_2$ in ethanol 5.285 ml (^{57}Fe 52.85 mg), ethylene glycol 50 ml and polyvinylpyrrolidone (PVP) 87.5 ml. A core is formed by conducting an electron beam investigation for 3 minutes in 10 MeV, 80 kGy, and 800 μA environments of the mixed precursors. Add 30 ml of ethylene glycol to 157.5 mg of platinum chloride ($PtCl_4$, F.W=336.9) to the electron beam investigation solution to form the shell. After that, an additional one-minute electron beam survey will be conducted in 10 MeV and 40 kGy environments, which have halved the century. After all the electron beam irradiation is dried to a powder, Fe@Pt/C is produced by heat treatment at 500℃ for 2 hours in an argon atmosphere after mixing with KB-600J using mortar. In the case of ^{57}Fe$_{1.5}$@Pt$_1$/C, the same synthesis process was carried out, but 3.955 ml (^{57}Fe 39.55 mg) of ^{57}FeCl$_2$ in ethanol was used.

2.2 Catalysts Characterization

^{57}Fe@Pt/C catalysts confirmed e-beam irradiation synthesis results using TEM and XRD. Through TEM ,^{57}Fe$_{1.5}$@Pt$_1$/C catalysts and ^{57}Fe$_2$@Pt$_1$/C catalysts formed a core-shell, respectively. The average particle diameter is 13.77 nm, 12.21 nm. Looking at the component distribution of each particle in EDS, ^{57}Fe$_{1.5}$@Pt$_1$/C catalysts to Fe and Pt were well synthesized in the core-shell position from ^{57}Fe$_2$@Pt$_1$/C catalysts. XRD measurements confirm that ^{57}Fe$_{1.5}$@Pt$_1$/C catalysts have better molecular formation than ^{57}Fe$_2$@Pt$_1$/C catalysts. As a result of checking the Fe@Pt content of the catalyst manufactured through thermogravimetric analysis (TGA), the total catalysts were 20 wt%.



2.3 Electrochemical analysis

CV experiments were performed to confirm the electrochemical surface area of the catalysts. In Fig. 1, the 0 to 0.3 V region is the adsorption and desorption area of hydrogen, and the 0.6 to 1 V region is the adsorption and desorption area of oxygen. Among them, looking at the 0 to 0.3 V region, it was confirmed that the hydrogen adsorption/desorption part of the $^{57}Fe_{1.5}@Pt_1/C$ catalysts was large.

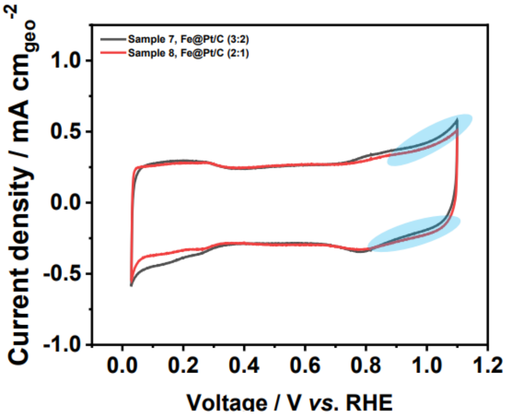


Fig. 1. Cyclic voltammograms of $Fe_{1.5}@Pt_1/C$ catalysts (black) and $Fe_2@Pt_1/C$ catalysts (red)

The electrochemical surface area (ESA) was calculated. The calculated ESA was 20.31 m2/g for $^{57}Fe_{1.5}@Pt_1/C$ catalysts and 22.72 m2/g for $^{57}Fe_2@Pt_1/C$ catalysts, and the surface part was smaller when the catalyst was produced by setting the ratio of Fe to 1.5:1.

An oxygen reduction reaction experiment was performed to evaluate the electrochemical activity of the catalyst. [Fig.2] The platinum catalyst has a slower oxygen reduction reaction than the hydrogen reaction rate. Therefore, the activity of the catalyst was confirmed through the oxygen reduction reaction rate. Compared with the existing research papers, it was confirmed that the activity was similar to that of the $^{57}Fe@Pt/C$ catalyst manufactured with E-beam.

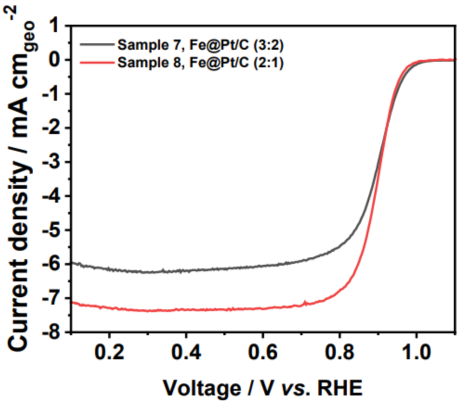


Fig. 2. Fraction of counts lost with voltage and charge sensitive preamplifiers as a function of the true count rate.

3. Conclusions

The performance comparison was performed by preparing a $^{57}Fe@Pt/C$ core-shell catalyst through E-beam irradiation and adjusting the ratio of Fe and Pt. The particle size and formation of the core shell were confirmed through TEM and XRD. In $^{57}Fe_{1.5}@Pt_1/C$ catalysts, the core shell was better formed than in $^{57}Fe_2@Pt_1/C$ catalysts, and the electrochemical surface area was also smaller. An oxygen diffusion reaction was performed to measure the activity of the catalyst. As the activity of each catalyst was similar to that of the previous paper, it was confirmed that the core-shell catalyst synthesis could be performed with the two-step E-beam irradiation.

The large particle size seems to have caused agglomeration of Fe due to heat treatment, etc., so it is determined that performance may be improved through acid treatment.

Acknowledgment

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