

^{57}Fe Mössbauer spectroscopy of Fe-N/C catalyst by ultrasonic and e-beam irradiation synthesis

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1. Introduction

Various non-noble ORR (oxygen reduction reaction) catalysts have been developed to replace expensive platinum-based catalysts. Fe-N/C is a low cost and excellent catalyst, and it has reported that the Fe and N precursor composite adsorbed on a carbon support produces an ORR catalyst with high activity and stability[1]. In developing high-performance catalysts, it is necessary to know the origin of catalytic activity and how the FeN_4 moiety contributes to the ORR mechanism.

Radiation-induced synthesis has many advantages in the use of irradiation techniques compared to conventional chemical methods. Therefore, we prepared the Fe-N/C catalyst using ultrasonic and electron beam(e-beam) irradiation.

^{57}Fe Mössbauer spectroscopy is a sensitive technique for the local structure of iron nuclei. It can be used as a characterization method to study the overall composition of Fe-N/C catalysts and in particular to distinguish between oxidation and spine states of similar FeN_4 environment[2]. We have investigated the temperature dependence of ^{57}Fe Mössbauer spectra of two Fe-N/C catalysts. The Mössbauer spectra of the two catalysts were measured between 4.2 and 295 K, and the parameters of the diverse Fe-based crystalline phases and moieties were obtained by fitting the spectra with suitable spectral components. In this work, we focused on the Fe-N/C catalyst according to the irradiation method(ultrasonic and e-beam) and studied the potential-dependent changes in the iron sites by Mössbauer spectroscopy.

2. Materials and Methods

^{57}Fe -N/C catalysts were synthesized by ultrasonic and electron beam irradiation. To obtain the Fe-N/C

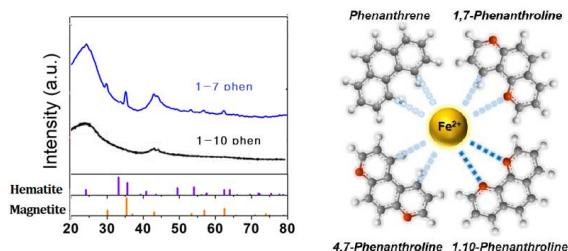


Fig. 1. XRD patterns of Fe-N/C catalysts prepared with different pore-fillers(1,7-Phenanthroline and 1,10-Phenanthroline).

catalysts, precursor solutions were prepared by mixing Fe precursor(^{57}Fe Chloride) with pore-filler (1,10-phenanthroline) in ethyl alcohol. Fig. 1 shows the XRD patterns of Fe-N/C catalysts prepared with different pore -fillers. Fe-N/C catalyst prepared using 1,10-phen than 1,7-phen pore-filler was successfully synthesized.

The formation conditions of the ^{57}Fe -N catalysts were confirmed by ultrasonic irradiation for 15 min or by irradiation at 80 kGy for 3 min using e-beam energy of 10 MeV and beam current of 800 μA . The precursor solution was stirred for allowing the complexes to adsorb onto the carbon support(Ketjen Black EC-600JD). The mixture was dried, and the solvent was evaporated. Finally, the dried powder was sintered at 800 $^\circ\text{C}$ for 1h under Ar atmosphere to obtain the ^{57}Fe -N/C catalysts.

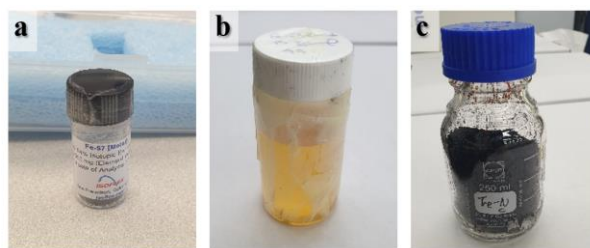


Fig. 2. a) ^{57}Fe Chloride precursor, b) ^{57}Fe Chloride and 1,10-phenanthroline in ethyl alcohol and c) ^{57}Fe -N/C catalysts.

The structural and morphological characterization of ultrasonic and e-beam irradiated ^{57}Fe -N/C catalysts were measured with Rigaku D/MAX 2500 X-ray diffractometer (XRD) using Cu $K\alpha$ radiation and JEOL-2200FS Transmission electron microscopy (TEM). The Mössbauer spectra were recorded with a Mössbauer

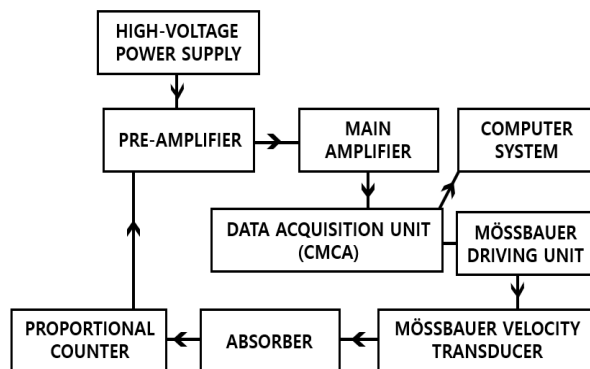


Fig. 3. Schematic diagram of transmission Mössbauer spectroscopy system.

spectrometer equipped with $^{57}\text{Co}/\text{Rh}$ source in transmission mode (Fig. 3). Measurements were performed at 295 K and the isomer shift was reported with respect to standard natural Fe-foil.

3. Results and Discussion

From the XRD results of the $^{57}\text{Fe-N/C}$ catalysts irradiated with ultrasonic and e-beam, the patterns of the two catalysts showed typical broad graphite C(002) and C(100) peaks. The TEM images show uniform particle size distribution and no agglomeration (Fig. 4).

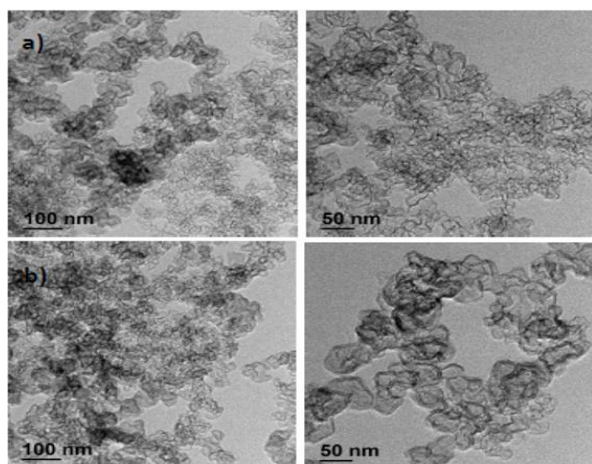


Fig. 4. TEM images of $^{57}\text{Fe-N/C}$ catalyst a) e-beam irradiation and b) ultrasonic irradiation.

The Mössbauer spectra were obtained at 4.2 and 295 K. The spectra of samples at 295 K consist of four doublets(D1~D4) and one single line(S1). The fitted Mössbauer parameters are assigned to the following iron species: D1- $\text{Fe}^{\text{II}}\text{N}_4$, $\text{Fe}^{\text{III}}\text{N}_4$, Fe/FeO cluster, D2-Intermediate spin $\text{Fe}^{\text{III}}\text{N}_4$, D3- $\text{Fe}^{\text{II}}\text{N}_4$, D4- Fe_3O_4 and S1-superparamagnetic $\alpha\text{-Fe}$. The spectrum of both catalysts can be fitted with FeN_4 sites and the same kind of inorganic iron species. Also, both samples were found to have about 20 % Fe_3O_4 present, as evidenced by the 4.2K data. The spectra at 4.2 K consist of three doublets(D1~D3), two sextets and one single line(S1). However, Fe_3O_4 , which is a doublet(D4) at 295K, appeared as a two sextets(tetrahedra A- and octahedral B-site) at 4.2K. From the Mössbauer spectra of the two catalyst, it can be seen that the irradiation method(e-beam or ultrasonic) has a slight effect on the quantity rather than the change for the iron species formed.

4. Conclusions

In this work, we have investigated of Mössbauer spectra of two $^{57}\text{Fe-N/C}$ catalysts. These measurements confirmed that the majority of the iron atoms were present in the catalyst in the form of FeN_4/C moieties containing iron in low or Intermediate spin states. These

results suggest that Mössbauer spectroscopy data serves as a complementary means to study the structure of the catalyst when studying the iron-based catalyst family.

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