Effect of plasma treatment on iron azaphthalocyanine-supported carbon materials

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Improving a catalytic activity of metal-supported carbon materials used in air electrodes for fuel cells or air batteries is a critical issue. Platinum has been used as a catalyst, however the cost of platinum is high. The development of non-rare metal catalysts is necessary.

Iron azaphthalocyanine (FeAzPc) has high catalytic activity for oxygen reduction reactions (ORR) and is a potential alternative to platinum [1]. The specific surface area and porous structure of the catalyst support have a significant influence on the number of active sites. In addition, an electrical conductivity of the catalyst support related to the electron transport in the catalyst layer. Thus, the material of the catalyst support plays an important role in the activity of the catalyst.

In this study, the effect of atmospheric pressure plasma (APP) treatment FeAzPc-supported carbon materials was investigated to improve the catalytic activity. In addition, the carbon materials as a catalyst support were compared between graphene oxide (GO) and ketjen black (KB). The GO or KB contain oxygen-containing functional groups and the reduction treatment by using the APP is performed to enhance the ORR activity.

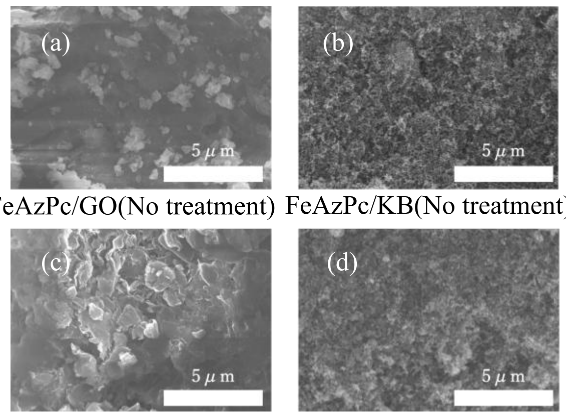
The FeAzPc dispersed in IPA and the GO dispersed in pure water were mixed. KB powder was added to the dispersion solution of FeAzPc. The weight ratio of FeAzPc/carbon materials for both catalysts was 1:0.5. The dispersion solutions were dried to obtain the FeAzPc/GO or FeAzPc/KB powders. The dried powders were treated by the APP for 120 minutes. The plasma was generated by applying an alternating voltage of 10 kV at 60 Hz between electrodes installed inside and outside the glass tube. A mixed gas of Ar/H_2 was flowed between the flowed into the glass tube at a flow rate of 2.5 slm and hydrogen gas flow rate ratio of 10%.

Figure 1 shows the plane view of SEM images of FeAzPc/GO and FeAzPc/KB. The prepared FeAzPc/GO is a sheet-like morphology as shown in Fig. 1(a) and the FeAzPc/KB is a powder-like morphology as shown in Fig. 1(b). These morphologies reflect the intrinsic structures of the respective carbon materials. The sheet-like structure of FeAzPc/GO was decomposed and the size was decreased with increasing the plasma treatment time, as shown in Fig.1(c). No significant morphological changes for FeAzPc/KB were observed, as shown in Fig. 1(d).

Figure 2 shows the Raman spectra of FeAzPc/GO and FeAzPc/KB. The D band around 1350 cm^{-1} indicates the defects of sp^2 structure such as graphene edges, in-plane lattice defects, and oxidation-induced damages. The G band around 1580 cm^{-1} is originated from planar sp^2-bonded carbon. The G band intensity to D band of FeAzPc/GO is stronger than that of FeAzPc/KB. This is due to the presence of graphene sheets of sp^2 carbon structure from GO, and KB consists of spherical particles with sp^2 carbon arrangements present only locally. The intensity ratio of the G band to the D band increased after the plasma treatment in both samples because the samples were reduced by the atomic hydrogen radicals produced by the plasma.

Reference

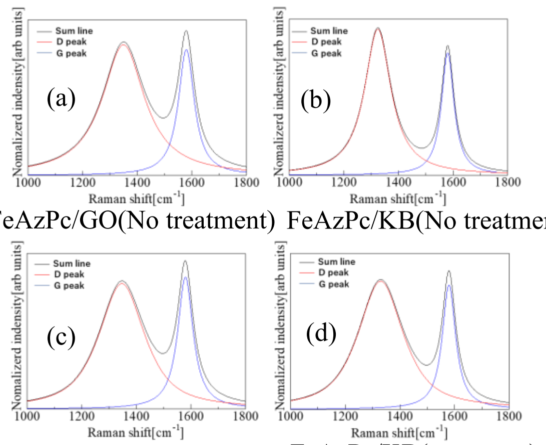
[1] H. Yabu, K. Nakamura, Y. Matsuo, Y. Umejima, H. Matsuyama, J. Nakamura, K. Ito, ACS Applied Energy Materials, 4, 14380 (2021).



FeAzPc/GO(No treatment) FeAzPc/KB(No treatment)

FeAzPc/GO(treatment) FeAzPc/KB(treatment)

Figure 1. SEM images of FeAzPc/carbon materials.



FeAzPc/GO(No treatment) FeAzPc/KB(No treatment)

FeAzPc/GO(treatment) FeAzPc/KB(treatment)

Figure 2. Raman spectra of FeAzPc/carbon materials.