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Plasma reduction of iron phthalocyanine-supported graphene oxide

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Carbon based catalysts have been used as air electrodes in fuel cells or air batteries. Platinum-supported carbon black catalysts have been widely used due to high oxygen reduction reaction (ORR) activity. The development of alternative catalysts has been studied due to high cost of platinum and low durability of carbon black. The iron phthalocyanine-supported reduced graphene oxide (FePc/rGO) is focused in this study due to high ORR activity [1][2]. It is necessary to remove oxygen functional groups such as epoxy groups from GO to activate the catalytic activity of FePc/GO. Hydrazine has been generally used for the reduction of FePc/GO, however, the use of hydrazine leads to serious risks to humans and the environment. The strong reducing species such as atomic hydrogen radicals or electrons are produced by an atmospheric pressure plasma (APP) and can be expected to provide significant reducing effect for FePc/GO.

In this study, FePc/GO was treated by the APP using hydrogen gas. The structural changes of FePc/rGO and the catalytic activity were investigated.

A solution of FePc powder dispersed in IPA was mixed with a solution of GO powder dispersed in ultrapure water at a ratio of 2:1. The solution was dried to synthesize FePc/GO powder of 30 mg, which was then treated with the APP. The APP was generated by applying an AC voltage of 10 kV at a frequency of 60 Hz between electrodes installed inside and outside the glass tube. An Ar/H_2 (10%) mixed gas was flowed into the glass tube at a flow rate of 2.5 slm.

Figure 1 shows the SEM image of the FePc/rGO. The synthesized FePc/GO consisted of FePc supported on sheet-like GO as shown in Fig. 1 (a). The sheet-like structure was decomposed and the size of GO was decreased with increasing the plasma treatment time to 90 min as shown in Figs. 1 (b) to (d).

Figure 2 shows the cyclic voltammetry (CV) curves for different plasma treatment time. The oxidation peak was observed at positive side of current density in the range from 0.7 [V vs. RHE] to 1.1 [V vs. RHE] and the reduction peak was observed at negative side of current density in the range from 0.05 [V vs. RHE] to 0.9 [V vs. RHE]. The peak current density of the oxidation peak increased from 0.1 mA/cm^2 to 0.7 mA/cm^2 at around 0.85 [V vs. RHE] with increasing plasma treatment time to 60 minutes, and the peak current density of reduction peak increased from -0.1 mA/cm^2 to -1.2 mA/cm^2 at around 0.65 [V vs. RHE]. These results indicate that the FePc/GO was reduced by the APP treatment. The current density decreased with increasing plasma treatment time more than 60 minutes. The size of GO was decreased with increasing the plasma treatment time as shown in Figs. 1, resulting that the conductivity of FePc/rGO decreases due to the disruption of electron conduction paths. The potential of the oxidation peak shifts from 0.8 [V vs. RHE] to 0.9 [V vs. RHE] and the potential of the reduction peak shifts from 0.72 [V vs. RHE] to 0.63 [V vs. RHE]. These shifts would cause an increase in overvoltage of fuel cells.

References

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[2] R. Cao *et al.*, Nat. Commun., 4, 2076 (2013).

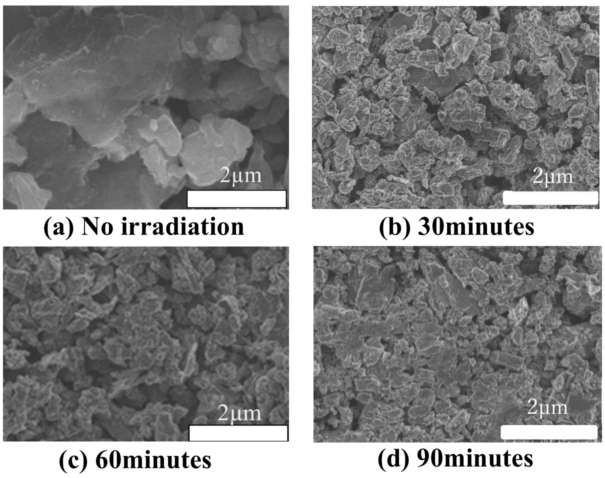

Figure 1 Plane view of SEM images of FePc/rGO for different treatment time.

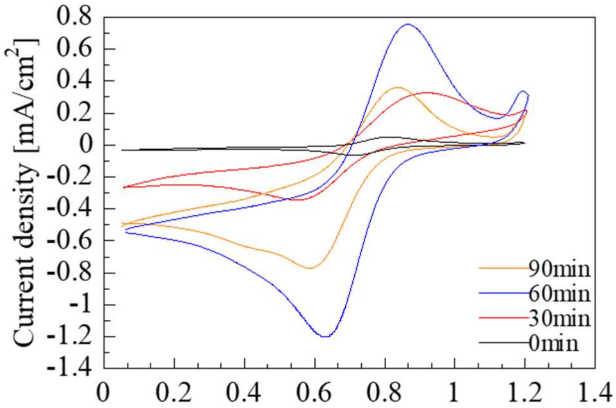

Figure 2 CV curves for different treatment time.