

ELECTROPHORETIC DEPOSITION OF METAL-PHTHALOCYANINE AS A HIGH-PERFORMANCE ELECTROCATALYST

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Key Words: Metal-phthalocyanine, Electrophoretic deposition (EPD), Oxygen reduction reaction (ORR), Gas diffusion type carbon electrodes (GDE).

Metal-phthalocyanines (MPc) has high chemical stability and high catalytic activities in electrochemical reactions such as oxygen reduction reaction (ORR), CO₂ reduction, and so on. It has becoming known that the catalytic activity of MPc should depend on the crystal structures, i.e., alfa-type MPc gives higher activity than other phases. In this study, the alfa-structure controlled MPcs could successfully be prepared by an electrophoretic deposition (EPD) method on gas diffusion type carbon electrode (GDE) as an electrocatalyst. Double layered MPcs electrocatalyst prepared by EPD also gave high performance for ORR.

MPc (M: Li, Mg, Mn, Fe, Co, Ni, Cu, Zn, Ag, Sn, Pb) was dissolved in dichloromethane solution with trifluoroacetic acid was used for EPD method at room temperature. GDE and Pt counter electrode were used EPD (DC: +40 - +100V, 1-10min). Crystal structures of the MPcs were investigated by XRD, UV-vis, SEM, FT-IR, etc. ORR properties were evaluated in a half-cell in 1M H₂SO₄ at 70°C with a potentiostat using reversible hydrogen electrode (RHE) and Pt plate as reference and counter electrodes, respectively.

Most of the alfa-phase MPcs could be prepared by the EPD on GDEs using dichloromethane solution containing trifluoroacetic acid. However, MPcs (M=Li, Mg) couldn't prepared by the same condition. Alfa-phase MPc doped GDE showed higher ORR activity than that of GDE loaded with beta-MPc. In the cathodic performance at 0.4 V vs. RHE ($i_{0.4}$) and open circuit potential (E_{ocp}) at 70°C of gas-diffusion electrodes loaded with various alfa-MPc catalysts deposited by EPD method. The GDEs loaded with alfa-MPcs showed various open circuit potentials, depending on the central metal (M) of alfa-MPc. GDE loaded with alfa-FePc showed the highest open circuit potential among the alfa-MPcs. This indicates that alfa-FePc could produce effect on density of adsorbed oxygen in the catalytic layer in the GDE. Moreover alfa-FePc based electrode showed high activity even at lower overpotential range, in spite of its low activity at higher overpotential range. The change in the Tafel slops was observed which indicates the change in the mechanism of ORR. Tafel slope of -43mV/decade at lower overpotential range shows the oxygen reduction reaction route with the formation of peroxo species in which the hydrogenation desorption reaction is rapid. While, the higher overpotential the Tafel slope of -222mV/decade might show the route which the peroxo species are not formed, like the H₂O₂ formation route. On the other hand, the Tafel slope of the GDE loaded with alfa-CoPc was not changed in the wide overpotential range. Also, the alfa-CoPc could keep the catalytic activity for several cycles of measurements of cathodic polarization curves, while that of alfa-FePc changed in the cycles. The decrease in ORR cycle for alfa-FePc seems to be come from the large strength of oxygen adsorption of alfa-FePc. On the other hand, CoPc/FePc double layered electrocatalyst prepared by the EPD gave more higher performance for ORR and stability.

Acknowledgment: This work was partially supported by the Grant from JST ACT-C and JSPS KAKENHI Grant Number 25410240.