

Introduction

For the widespread commercialization of Polymer Electrolyte Fuel Cell (PEFC), reducing the amount of platinum used for cathode catalyst material is important by improving the oxygen reduction reaction (ORR) activity. Convection voltammetry using rotating disc electrode (RDE) is one of the usable ways for evaluating ORR activity of cathode catalyst materials for PEFCs. However, the correlation between ORR activity and the electronic as well as local structure of these materials casted on Membrane Electrode Assembly (MEA) have not been fully understood yet. In this paper, we report *in-situ* study of Pt/C catalysis (T.K.K.) in MEA by newly developed XAS cell. We investigated the correlation with the electronic structure (XANES) / local structural parameters (EXAFS) of the Pt/C catalyst and investigated the factors that govern the oxygen reduction reaction activity on Pt surface.

Experimental methods

MEA was prepared using platinum-supported carbon (Pt/C, T.K.K) as a cathode catalyst and Pd/C as an anode catalyst. A precisely temperature/humidity-controlled electrochemical cell was newly developed for our experiment. The measurements were carried out at 60-80 °C-85%RH. Pt L_{III, II}-edge XAS were collected by using BL01B1 at SPring-8 (Japan). The measurements were performed by a transmission mode. The number of Pt 5d orbital vacancies was calculated from the obtained XANES and the local structure of Pt was analyzed from EXAFS.

Results and discussion

According to XANES results, oxidation at Pt surface dramatically increased at high temperature in 80 °C at 1.1 V. This oxygen species could reduce the ORR by blocking active sites for additional O₂ adsorption. We also found the rapid increase of Pt 5d orbital vacancy by X-ray absorption spectra with the temperature, indicating that Pt was more easily oxidized at 80°C than 60 °C.

Conclusion

We report *in-situ* study of Pt/C catalysis (T.K.K.) in MEA by using newly developed XAS cell and investigated the correlation with the electronic structure (XANES) / local structural parameters (EXAFS) of the Pt/C catalyst. It was found that the rapid increase of Pt 5d orbital vacancy with the temperature, indicating that Pt was more easily oxidized at 80°C than 60 °C.

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