学 位 論 文 内 容 の 要 旨

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学 位 論 文 題 名

XAFS studies on the well-defined fuel cell model catalysts

(燃料電池モデル触媒の XAFS 研究)

To meet the target of carbon neutralization society and solve the critical issue arising from the depletion of traditional fossil storage and high demand for renewable energy resources, fuel cell technology provides a promising solution to the problems. Oxygen reduction reaction (ORR) at cathode side of fuel cells is the crucial rate determining step, which is accelerated by the monometallic Pt and bimetallic Pt-based PtM (M=Pd, Au, etc) alloy nanoparticles (NPs) catalysts supported on porous carbons. In order to increase the activity and durability and to further contribute to the development of fuel cell, it is significantly important to investigate the relationship between the electronic and geometric structures of Pt (PtM) nanoparticles and their activities. Nevertheless, these porous carbon powder catalyst supports usually exhibit an ill-defined structure, which is hard to give an exact description of structure and related active sites. An alternative way is to use a model catalyst system to make it possible to apply surface science techniques to reveal the detailed structures at atomic scales. Furthermore, in situ characterization must be necessary to obtain precise insights into real reaction processes. X-ray absorption fine structure (XAFS) is the most suitable surface science technique, which allows us to carry out in situ characterization of electronic and geometric structures of Pt (PtM) NPs on atomic level. However, when I tried to apply it to the model systems, new developments in XAFS techniques are needed. In this work I developed three new XAFS techniques: a bent crystal Laue analyzer + back illuminated / high energy resolution fluorescence detection X-ray absorption fine structure (BCLA+BI/HERFD-XAFS), BCLA enhanced polarization-dependent total reflection fluorescence XAFS (BCLA+PTRF-XAFS) technique, and in situ electrochemical PTRF-XAFS (EC-PTRF-XAFS) technique. These new XAFS techniques are applied to the Pt-based model systems. I found several new and important concepts for the development of noble metal Pt-based ORR catalysts.

The first chapter gave a general introduction.

The second chapter described experimental methods and analysis details, which included model catalyst preparation for monometallic (Pt) and bimetallic Pt-based (PtM) catalyst systems, development of in-situ electrochemical XAFS apparatus, and related surface science characterizations.

The third chapter described the investigation of model catalyst structure for monometallic Pt NPs in a

small amount (10^{15} Pt atoms cm^{-2}) supported on the flat HOPG. A novel BCLA/HERFD-BI-XAFS method was applied for the structure study under in-situ conditions which corresponded to the ORR reactions. Structure framework and surface adsorbates were successfully investigated.

The fourth chapter focused on the development of in-situ EC-BCLA+PTRF-XAFS measurement apparatus for structure studies of diluted noble metals supported by single crystal surfaces. The limited target element amount and enormous elastic scatterings arises from solutions hinders the in-situ EC-XAFS studies. The applications of BCLA perfectly solved abovementioned problems with delicate adjustment between the BCLA position and X-ray footprints, especially for EXAFS of bimetallic PtAu system, for which elements possess a close absorption energy edge under solution appeared conditions.

In the fifth chapter, I successfully applied the in-situ EC-PTRF-XAFS method to the bimetallic Pt-based model catalyst system of Pt sub-ML supported by Au (111). The development of total reflection and application of thin electrolyte ensured the limited scatterings from solution layer. The polarized measurement provided 3D structure information for Pt-Pt and Pt-Au bond distance determination.

The sixth chapter gave the general conclusion of the dissertation. I successfully developed three XAFS methods suitable for structure investigation of monometallic and bimetallic Pt-based model catalysts for ORR under in-situ conditions. I found the origin for high activity and long duration of Pt based model catalysts, which will contribute to the development of the high-performance ORR catalysts.