MERIT Internship Program (Domestic) Report

Merit 8th

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Host institute : Nissan Arc Co., Ltd. Device analysis unit

Period : November 1st, 2019 ～ January 15th, 2019

Theme : Acquisition of DFT calculation and Synchrotron radiation experiment

Research contents and results：

The polymer electrolyte fuel cell (PEFC) is one of the most promising fuel cells due to its low operating temperature and compactness. Usual PEFCs employ metal catalysts as electrodes and the activity or durability of those catalysts have been studied intensively. Recent researches have revealed that the metal sheet catalysts have larger specific surface area and longer durability compared to the conventional metal particle catalysts, and thus the sheet catalysts have gained special attention. In this internship, we have conducted research on Ru and Pt nanosheet catalysts which are provided from one of the partner institutions of the Nissan Arc Co., Ltd. by the means of both DFT calculation and synchrotron radiation experiment.

In DFT calculation, we compared two models representing a Ru nanoparticle catalyst and a Ru nanosheet catalyst consists of 2 or 3 Ru atomic layers. Among Ru nanosheets and nanoparticles, only nanosheet catalysts have been known to have reversible redox reactivity, i.e. reactivity to reduction process by decreasing the electric potential even after they get oxidized. Since this reversible redox reaction is closely related to the high durability of Ru nanosheets, the clarification of the mechanism of the redox reaction has been in need. Oxidized Ru in general is known to possess a subsurface, namely, an interlayer of O atoms between the surface and the second layer of Ru. If we focus on an O atom absorbed in a Ru subsurface in the oxidization process, the reduction reaction can be interpreted as the movement of O atoms from the subsurface to the surface and eventually to the infinity. We firstly divided this series of movements to several steps and then calculated the energy barrier of each step. The two models mentioned above were created by *Material Studio* owned by Nissan Arc Co., Ltd. and VASP was operated as a DFT calculation program. As a result, we verified that in every steps of the reduction reaction of Ru, the energy barrier of the nanosheet was lower than that of the nanoparticle, which implies that reduction reactions tend to occur easily in nanosheets in comparison to nanoparticles. In addition, we confirmed the same result with more realistic models of a nanosheet and a nanoparticle which have defects in the Ru surface. These results support the previous reports that only Ru nanosheets have the reversible redox reactivity. We attribute this phenomenon to the observation that the coordination number of an O atom in the subsurface of the nanosheet is smaller than that of nanoparticle, which means the degree of binding of the O atom is also smaller in the nanosheet.

In the synchrotron radiation experiment, we measured a Ru@Pt core shell nanosheet sample which consisted of a Ru nanosheet surrounded by a few Pt atomic layers. We examined how the sample was toxified by CO atmosphere by XAFS measurement in Spring-8. The hydrogen air used in a fuel cell sometimes contains toxic CO which deteriorate the catalysts by occupying the active site on them. Since Ru@Pt core shell nanosheet catalysts had been synthesized recently, their tolerance against the CO toxification was one of the measure characteristics which should be clarified. We had expected to see the CO absorption dependence in Pt L3 edge spectra XANES and EXAFS results, however, no sizable difference depending on the CO absorption was detected unfortunately. On the other hand, the result showed the absorption dependence of the K edge spectra of Ru, which should be only in the core and on which no CO would adhere directly. The oxidation of Ru is suppressed with CO adsorption.

According to Ru K edge spectra EXAFS results, the intensity of the peak corresponding to the Ru-C bonds increased in CO atmosphere, leading to the suppression of Ru oxidization. These results suggest that the sample we measured might have not had the structure we supposed and thus further detailed analysis on its structure is awaited.

Impression：

One of the attractive points of analytic companies is that all the researchers can fully utilize their expertise in their tasks every day. At the same time, since the best method or technology changes each time depending on what customers need, it is required for employees to keep studying hard to achieve new knowledge. Such kind of efforts of learning new things always help push one’s boundaries of possibility and I felt that the analytic company offer the ideal circumstance for that. This internship motivated me to analyze more and more companies or research institutes to compare their advantages and disadvantages for my future carrier selection.

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