The study on crystal structures and catalytic activity of Pt-Co nanoparticles for oxygen redox reaction by in-situ X-ray diffraction

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We report results of synchrotron X-ray diffraction measurements on the Pt and Pt-Co nanopartiles to understand the catalytic activity for oxygen reduction reaction related to the micro and macro structure of the nanoparticles. We employed synchrotron radiation at BL02B2 under proposal number 2007B1774. Carbon supported Pt-Co nanorpaticles with averaged particle size of 2 - 4 nm has been studied. It has been confirmed that Pt-Co nanoparticles have more uniform Pt-Co composition after annealing at 1000 K under vacuum with some extend of size distribution. Smaller size of Pt-Co nanoparticles contain less Co compared to larger nanoparticles. These results are well agreed with the observation on individual nanoparticles by STEM / EDX, suggesting Pt segregation after annealing for Pt-Co nanoparticles.

Fuel cell can provide a clean, sustainable, and efficient energy solution for transportation and large-scale chemical energy storage, provided that the fuel is produced from renewable energy sources. Noble metals such as Pt and Pt-based alloys are required for oxygen reduction at the cathode to achieve high conversion efficiencies and power densities needed for practical applications, particularly for transportation. To maximize the surface area of Pt-based alloys and to minimize the loading weight, a nanoparticle catalyst on the order of 2-3 nm in diameter are used.

As one of the Pt-based nanoparticles, Pt-Co nanoparticles have been studied by several research groups. Pt-Co nanoparicles show smaller overpotential than Pt nanoparticles based on the surface area of the nanoparticles. When the Pt_3Co nanoparicles are heated under vacuum condition at 1000 K, the Pt_3Co oxygen reduction activity based on the surface area is further improved. Figure 1 shows synchrotron X-ray diffraction patters of Pt and Pt-Co nanoparticles. As can be seen in Figure 1, Pt nanoparticles (2 nm of average size observed by TEM) shows not well defined peak profile. After the annealing at 1173 K, it has been found that the peak profile changes into triangular shape, which can be explained by that nanoparticles own a wider particle size distribution. Although the trend of growth of particle size and the distinct size distribution after the annealing is similar with the Pt nanoparticles, detailed analysis for the Pt_3Co nanoparticles further revealed that 1) the nanoparticles own not only distinct particle size but also clearly different lattice parameters, 2) a Cu_3Au-type ordered arrangement with space group symmetry Pm-3m can be confirmed, which is originated mostly from nanoparticles and partly from merged and well-grown particles after annealing. The clear correlation between particle size and lattice parameters has been also found as shown in Figure 2. This can be explained by the dependence on the particle size to the chemical composition: smaller size of particles has less Co in comparison of larger size of nanoparticles, which is further confirmed by STEM/EDX study for individual nanoparticles. The Pt/Co ratio distribution for all of nanoparticles becomes uniform after annealing, and averaged lattice parameters become small for the most of nanopartilces. From these results, we conclude that enlarged Pt-Pt interatomic distances in average are involved in the enhanced oxygen reduction activity. Currently, we are trying to prove the enhanced oxygen reduction activity related to not only the change in the interatomic distances but also surface structures in an atomic scale and electronic structures of the nanoparticles. The all of results, including synchrotron XRD works, will be published in the near future.

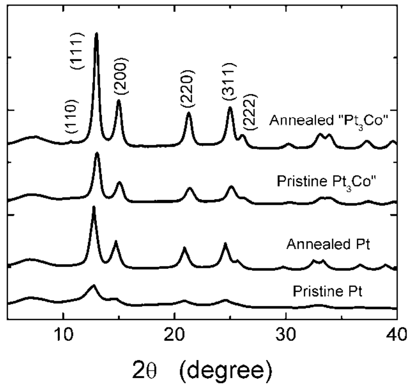

Figure 1 Synchrotron X-ray diffraction patterns of pristine Pt and Pt-Co nanoparticles and the annealed nanoparticles.

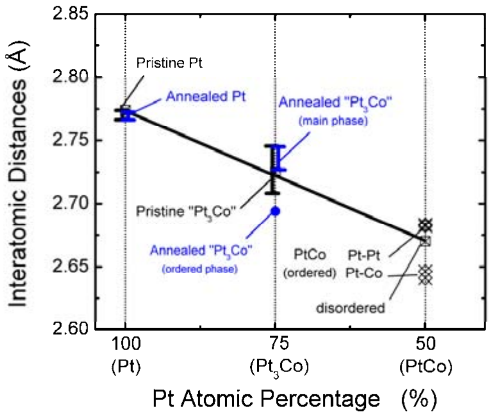

Figure 2 The change in the interatomic distances of Pt and Pt-Co nanoprticles. Annealed “Pt3Co” shows narrower lattice parameter distribution than Pristine samples with Au3Cu-type ordered phase.