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in situ Electrochemical XAFS Study on ORR Activity and Degradation Behavior of Core-Shell Catalyst

Xiaoming Wang[1], Yuki Orikasa[1], Yuki Takesue[2], Hideo Inoue[3], Masashi Nakamura[2], Taketoshi Minato[4], Nagahiro Hoshi[2], and Yoshiharu Uchimoto[1]
[1]Graduate School of Human and Environmental Studies, Kyoto University, Sakyo-ku, Kyoto 606-8501, Japan
[2]Graduate School of Engineering, Chiba University, Inage-ku, Chiba 263-8522, Japan
[3]Ishifuku Metal Industry Limited Company, Soka, Saitama 340-0002, Japan
[4]Office of Society-Academia Collaboration for Innovation, Kyoto University, Uji, Kyoto, 611-0011, Japan

Recent concerns on global warming and the depletion of petroleum resource lead to a great demand to commercialize clean energy-conversion technologies such as polymer electrolyte fuel cells (PEFCs). One challenge for commercialization of fuel cells is the discovery of highly active and considerably cheap Pt catalysts for oxygen reduction reaction (ORR), and still has no great strides. The monolayer Pt catalysts provides a promising approach for the sustainable use of PEFCs where the employment of core materials remarkably decrease the expensive cost of Pt cathode catalysts and significantly increase the slow kinetic activity toward ORR.[1] Herein, the key role of core materials in controlling the activity of monolayer Pt catalysts is to induce the strain effect, tensile or compressive, in which the resulting d-band center shifts as a major factor determine the activity of catalysts.[2] Nevertheless, a quantitative correlation between them remains unclear. Monolayer Pt catalysts with uniquely catalytic properties toward ORR can be created by tuning the structure of core materials.[3] Several investigations have been carried out to resolve the role of core structure in the catalytic activity of monolayer Pt catalysts toward ORR; a definitive determination, however, still remains elusive. In this work, based on extended X-ray absorption fine structure (EXAFS) analysis of monolayer Pt atoms on various Pd single crystal facets, we propose a general methodology for evaluating the lattice strain of monolayer Pt shell on Pd core nanoparticles. And then, we investigate the lattice strain of monolayer Pt shells on a variety of Pd nanoparticles. Further, the lattice strain dependence of the resulting ORR activity has been studied.[4]

We prepared the monolayer Pt on Pd single crystals of (111), (100) and (110) facets. Pt L_{III}-edge EXAFS was investigated under *in situ* condition. The employment of the standard monolayer Pt samples demonstrates that the self-built structural model of monolayer Pt shell on Pd single crystal (111) facet is undoubtedly available. And, the self-built structural model can include all structural information of the nearest neighbors in monolayer Pt shells on Pd single crystal (111), (100) and (110) facets. Thus, via the general structural model of monolayer Pt shell on Pd single crystal (111) facet, EXAFS fitting of monolayer Pt shell on core nanoparticles with the short range ordering structure is facile to be performed.

The quantitative lattice strain of monolayer Pt shells provides a tangible understanding on their different ORR activity and the dependent correlation (Fig. 1) between lattice strain and the corresponding specific activity (at 0.90 V vs. RHE) calculated from Koutecky-Levich equation. As shown in Fig. 1, the compression of Pt-Pt bond distance induces a remarkable increase in the specific activity toward ORR. Compared to the commercial Pt nanoparticles (0.20-0.25 mA cm^{-2}),[5] the greatest monolayer Pt shell induces a three-time increment in the specific activity. More importantly, these enhanced specific activities show a linear dependence on the lattice strain. Our quantitative correlation is also in good agreement with the theoretical explanation of the d-band model developed by Nøskov and co-workers.[6] The strain effect induced d-band shift is related to the adsorption properties of rate-limiting intermediates in catalytic processes to the electronic structure of the catalyst. Thus, in our experiments, the augment of the compression extent of Pt-Pt bond distance will generate a highly catalytic activity toward ORR. It should be noted, as for the eventual conclusion about the optimal lattice strain of monolayer Pt shells, a tailoring of monolayer Pt structure is beyond the scope.

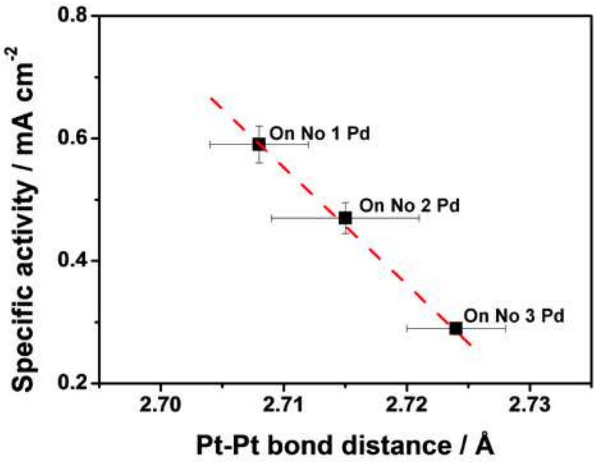

Figure 1. Lattice strain dependence of monolayer Pt shell specific activity (at 0.9 V vs. RHE) toward ORR. (Size of Pd particles, No. 1: 3.5 nm, No. 2: 3.9 nm, and No. 3: 5.7 nm.)

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5. References

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