

Exploring the Structural Degradation of Monolayer Pt Shell Catalysts in Oxygen Reduction Reaction Based on in situ X-ray Absorption Spectroscopy

Xiaoming Wang[†], Tsukasa Nakai[†], Yuki Orikasa[†],
Taketoshi Minato[‡], and Yoshiharu Uchimoto[†]

[†]Graduate School of Human and Environmental Studies,
Kyoto University, Sakyo-ku, Kyoto 606-8501, Japan

[‡]Office of Society-Academia Collaboration for
Innovation, Kyoto University, Uji, Kyoto, 611-0011,
Japan

1. Introduction

The commercialization of polymer electrolyte membrane fuel cells (PEMFCs) depends on heavily significant improvement of the cathodic activity and stability toward oxygen reduction reaction (ORR) [1-3]. Recently, the rise of monolayer Pt shell catalysts with the compressible lattice strain provides a promising approach to reduce Pt usage and enhance Pt catalysis toward ORR. Considering their practical application in PEMFCs, the structural degradation in monolayer Pt shell arouses tremendous interest due to its significance for the catalytic performance in fuel cells. For conventional carbon-supported Pt nanoparticles (Pt/C), previous publications have provided a basis for the understanding of their degradation mechanisms [4]. In contrast to Pt-based nanoparticles, the structural degradation of Pt monolayer Pt shell catalysts lacks a systematic and profound study. Among the previous publications [5-7], only the accelerated cyclic voltammetry and the combined scanning transmission electron microscopy have been used to qualitatively study the degradation of monolayer Pt shells. For conventional techniques, it's not easy to observe the degradation process of monolayer Pt shell. In this work, we're addressed in Pd core-Pt shell catalyst (Pt/Pd/C) and monitor monolayer Pt shell degradation during cyclic staircase voltammetry of redox process using in situ X-ray absorption spectroscopy (XAS).

2. Experimental

Monolayer Pt shell catalyst on Pd core nanoparticles is synthesized using monolayer Cu mediator method. The structural degradation is induced by cyclic staircase ranging from 0.5 to 1.15 V vs. RHE in O₂-saturated HClO₄ solution using in situ XAS. Using a potentiostat, we controlled the potential, obtained steady-state, and then, collected XAS spectrum. The measurements were done at the beamline BL01B1 and BL14B2 at SPring-8. The L_{III} and L_{II} absorption edge spectra of Pt were measured in fluorescence mode using a self-designated in situ electrochemical cell.

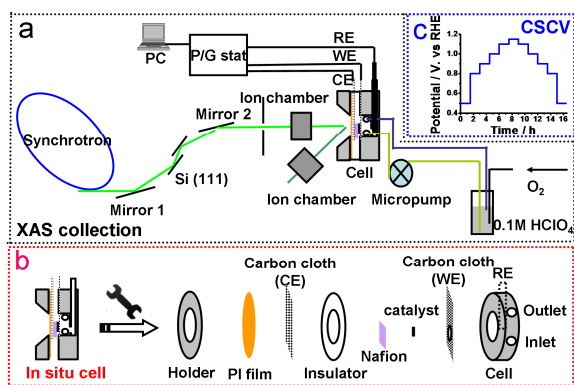


Fig.1. Scheme of experimental

3. Result and discussion

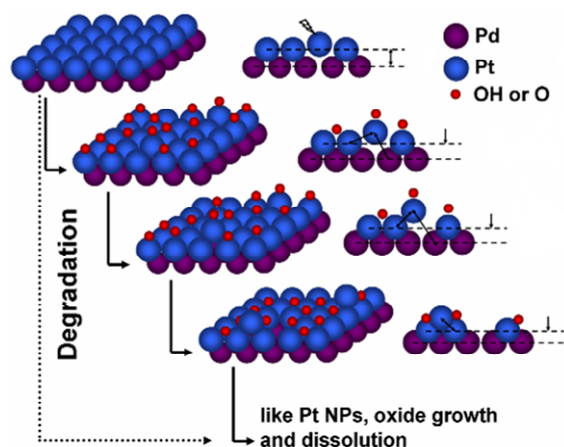


Fig.2. Simple scheme of monolayer Pt shell degradation.

Fig.2. shows scheme of monolayer Pt shell degradation proposed our measurement result. We suggest that, proceeding degradation process, core shell catalyst Pt leave from Pd because of degradation, agglomerate on Pt nanoparticle, and then, form the pseudo Pt nanocrystal. Therefore, Pt-Pd interaction weakened and oxidized species easily adsorbed to the newly formed Pt nanoparticle. Finally, the irreversible structure formed.

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5. References

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