Oxidative surface roughening of Pt electrode depending on electrolyte cations

The formation of surface oxides on solid metal electrodes, which affects the activity and selectivity of electrocatalytic reactions, is a primary concern in the development of high-performance electrocatalysts. Platinum (Pt) is a fundamental cathode element for low-temperature fuel cells owing to its exceptionally high activity in the oxygen reduction reaction (ORR). The roughening and dissolution of the surface atomic layer induced by oxide formation and reduction results in a restructuring of the surface morphology, which governs the ORR activity and durability. At positive potentials, where the irreversible surface oxidation of Pt occurs, the place exchange of surface Pt atoms with oxygen atoms is induced, forming a complex Pt oxide. The ions in the electrical double layer (EDL) affect the surface oxidation of the Pt electrode. In a LiOH solution, the stable adsorbed hydroxide (OH_{ad}) interacting with hydrophilic Li^+ inhibits further oxidation of Pt(111), whereas in a CsOH solution without hydrophilic cations, the absence of stable OH_{ad} results in surface roughening [1]. Hydrophobic cations are effective for ORR activation [2]. Surface oxidation in the presence of hydrophobic cations is interesting owing to the compatibility between activity and stability of electrocatalysts in alkaline media. Determination of the detailed interfacial structure provides insights into the EDL structure for highly active and durable electrocatalysis under oxide formation/reduction conditions. In this study, three-dimensional structural determination using *in situ* X-ray diffraction revealed that the hydrophilicity/hydrophobicity of cations at the interface plays an essential role in oxide formation.

X-ray diffraction (XRD) was performed using SPring-8 **BL13XU** with an X-ray energy of 20 keV. Structural analysis along the surface-normal direction was conducted using X-ray specular crystal truncation rod (CTR) scattering, which reflected the atomic structure along the out-of-plane direction. The specular CTR profiles were obtained between 0.5 and 1.2 V (RHE) in 0.1 M KOH and tetramethylammonium hydroxide (TMAOH), as shown in Fig. 1(a). The atomic-scale structures of Pt(111) in KOH and TMAOH

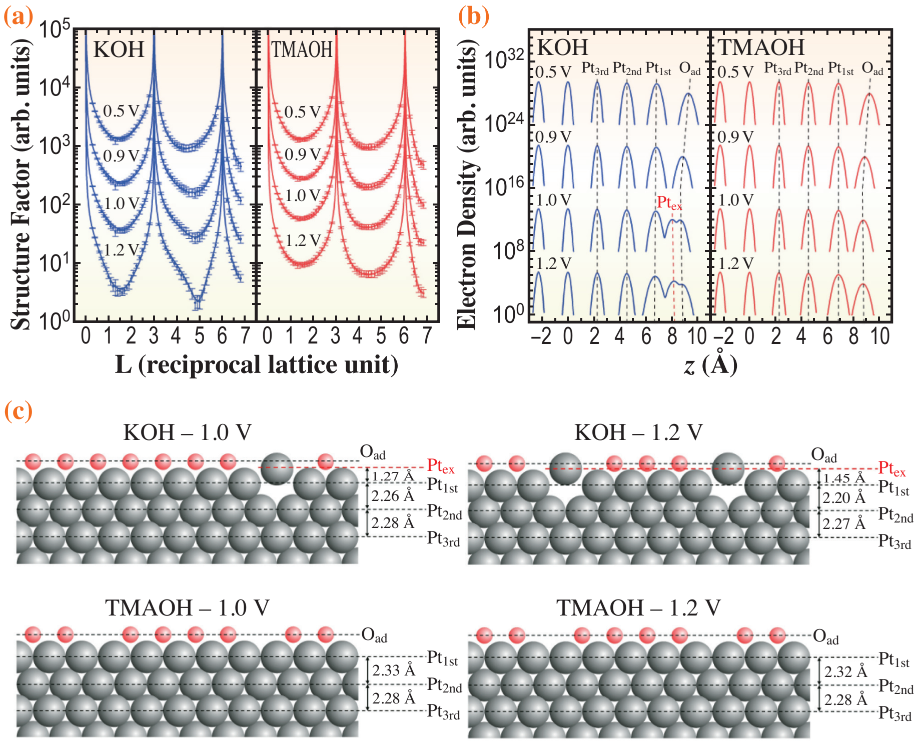

Fig. 1. **(a)** Specular CTR scattering profiles of Pt(111) in 0.1 M KOH and TMAOH. The dots and the solid lines represent the experimental data and the structure factors calculated from the optimized model, respectively. **(b)** Electron density profiles of Pt(111) along the direction normal to the surface calculated from the optimized model. **(c)** Side view of the optimized structure of Pt(111) in 0.1 M KOH and TMAOH.

solutions were determined by optimizing a model consisting of three layers of Pt and a monolayer of adsorbed oxygen to fit the CTR profiles. The vertical atomic position, occupancy factor, and Debye–Waller factors of the Pt and oxygen layers were optimized using the least-squares method. The electron-density profiles and schematic models of the interfacial structure are shown in Figs. 1(b) and 1(c), respectively.

At 0.5 V, the distance between the first Pt (Pt_{1st}) and adsorbed oxygen (O_{ad}) layers was approximately 2.4 Å in both solutions, corresponding to the oxygen atoms of the adsorbed water. The layer distance between Pt_{1st} and the second Pt (Pt_{2nd}) was approximately 2.32 Å in both solutions, which represents a 2% expansion compared to the value in the bulk. The interaction between the Pt surface and adsorbed water weakened the bonding between Pt_{1st} and Pt_{2nd}, resulting in surface relaxation of the Pt_{1st} layer. At 0.9 V, the Pt_{1st}–O_{ad} distance contracted to ~2.0 Å in both solutions due to the formation of an adsorbed OH_{ad} layer, assumed to be the major adsorbed species on Pt(111). Additional electron density resulting from the extracted Pt atoms (Pt_{ex}) appeared at 1.27 Å from the surface in KOH at 1.0 V, representing the precursor of place exchange. At the more positive potential of 1.2 V, the Pt_{1st}–Pt_{ex} distance expanded to 1.45 Å, and the coverage of the Pt_{ex} layer reached 0.18 in KOH. By contrast, no significant changes were observed in the interfacial structure of TMAOH up to 1.2 V.

Figure 2 shows the X-ray diffraction intensity during the anodic and cathodic scans at the reciprocal lattice position of (0 0 1.5), which is sensitive to surface roughness. In KOH, the intensity between Bragg peaks decreased above 0.9 V during the anodic scan. The diffraction intensity gradually decreased with potential cycling, suggesting that the reduction of surface Pt oxides irreversibly roughened the surface. Conversely, in TMAOH, the diffraction intensity slightly decreased above 1.0 V but recovered during the cathodic scan to 0.05 V, and remained independent of potential cycles. Hydrophilic Li^+ strongly stabilizes OH_{ad}, hindering the extraction of surface Pt atoms (Fig. 3). Interestingly, bulky hydrophobic cations, such as TMA^+, also reduce irreversible oxidation despite the absence of strong interactions with OH_{ad}. Hydrophobic TMA^+ inhibits the formation of complex Pt oxides associated with Pt extraction. By contrast, the moderate hydrophilicity of K^+ has no protective effect against irreversible oxidation. Moderate hydrophilicity enabled the formation of a complex Pt oxide layer (Fig. 3). The electrostatic repulsion in this complex oxide layer promotes Pt extraction.

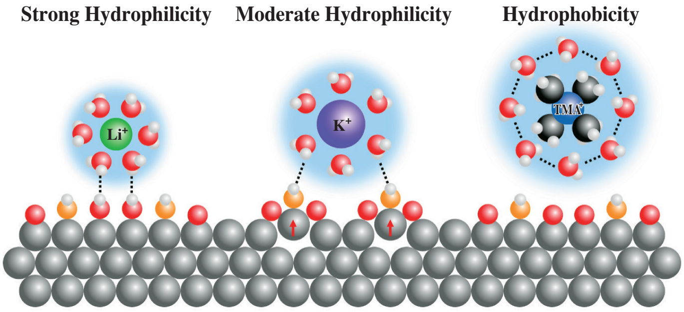

Fig. 3. Schematic model of the interfacial structure of Pt(111) in LiOH, KOH, and TMAOH solutions. The black dots and red arrows denote the noncovalent interactions and surface extraction, respectively. The gray, red (orange), and white balls represent platinum, oxygen, and hydrogen atoms.

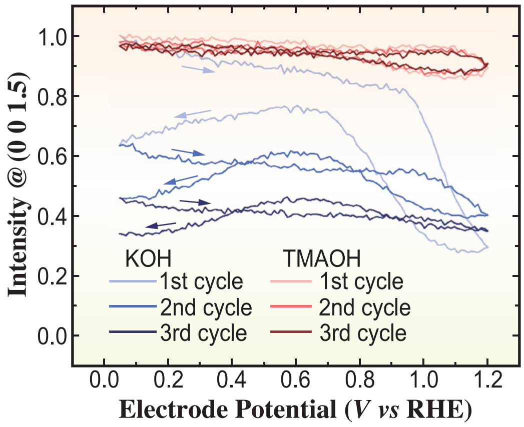

Fig. 2. Potential-dependent X-ray diffraction intensity at the reciprocal lattice position of (0 0 1.5) in 0.1 M KOH and TMAOH. The scan started from 0.05 V to the positive direction with a scanning rate of 0.002 Vs^{-1}.

Tomoaki Kumeda and Masashi Nakamura*

Graduate School of Engineering, Chiba University

*Email: mnakamura@faculty.chiba-u.jp

References

[1] M. Nakamura *et al.*: ChemPhysChem. **14** (2013) 2426.
[2] D. Strmcnik *et al.*: Nat. Chem. **1** (2009) 466.
[3] *T. Kumeda, K. Kondo, S. Tanaka, O. Sakata, N. Hoshi, M. Nakamura: J. Am. Chem. Soc.* ***146*** *(2024) 10312.*