Real-Time Monitoring of Electrode Surface Structure during Electrochemical Reaction

A high-speed surface X-ray diffraction measurement method, which uses wavelength-dispersive convergent X-rays and a two-dimensional detector, succeeds in capturing electrochemical processes on a Pt(111) electrode surface on a time scale of seconds and less. During the electrochemical oxidation of methanol, a transient vertical displacement of the Pt(111) surface atomic layer is revealed, indicating a process of oxidative stripping of CO poisoning layer.

Methods for observing solid-liquid interfaces have been developed over several decades, motivated by many important phenomena such as electrochemical energy conversion. The electrochemical reactions consist of various elementary steps such as adsorption/ desorption and oxidation/reduction of reactants and formation/destruction of interface layer. Many efforts have been made to understand the interface mechanisms, aiming to improve the energy conversion efficiency. Novel in-situ techniques, which are capable of determining atomic or molecular and electronic structures, are very helpful in understanding the interface mechanisms. However, capturing the dynamics with a sufficient temporal resolution remains challenging.

X-ray crystal truncation rod (CTR) scattering is a unique and nondestructive technique for determining the atomic structure of buried interfaces and has been used for studying electrochemical interfaces. The method is often limited to the analysis of static structures because the data acquisition of a CTR profile takes several tens of minutes or more, which in most cases, is longer than the relaxation time of the structural changes. A new high-speed method has been developed to acquire a wide range of CTR profile at once within few seconds or less [1]. The method uses energy-dispersive convergent X-rays instead of the conventional monochromatic collimated X-rays. As shown in **Fig. 1**, the combination of the energy-dispersive X-rays and a two-dimensional (2D) detector allows for a single acquisition of the CTR profile without moving the specimen and detector, enabling the real-time monitoring of the interface phenomena [2].

The high-speed technique was used to capture the atomic-scale phenomena at the electrochemical interfaces [3]. The time evolution of CTR profile was measured during electrochemical decomposition of methanol on a Pt catalyst electrode, which is the key electrochemical reaction of a direct methanol fuel cell. It is known that methanol is decomposed to CO molecule immediately after being adsorbed on the Pt surface. The CO molecules are strongly adsorbed on the Pt surface and cover most of it resulting in a serious reduction in its methanol decomposition efficiency (CO poisoning). The clear relationship between the CO poisoning and catalytic activities was successfully illustrated by realtime monitoring.







Figure 2: (a) Vertical displacement of the surface atomic layer of the Pt(111) electrode in the methanol solution during potential scan. (b) The reaction current from the Pt(111) electrode [3].

Figure 2 displays the vertical displacement of the surface atomic layer of the Pt(111) electrode during cyclic voltammetry (CV). When the potential is below 0.4 V (vs. reversible hydrogen electrode (RHE)), the surface is covered with the CO and the Pt surface layer is lifted up by about 0.11 Å due to the interaction with CO. When the potential is increased above 0.6 V [Fig. 2(a)], the Pt surface layer starts relaxing and the oxidation current increases simultaneously [Fig. 2(b)], representing the oxidative desorption of CO (CO + OH \rightarrow CO₂ + H⁺ + e⁻) and the abrupt increase in methanol oxidation activity. In the negativegoing potential scan, the Pt surface is again poisoned by CO with a pathway different from the positive-going scan. The hysteretic structural change that can only be observed by real-time monitoring, clearly demonstrates that the CO desorption is the rate-determining step of methanol decomposition.

The time-resolved analysis indicates the CO desorption process. **Figure 3** shows the time evolution of the Pt surface layer displacement after the potential steps up from 0.0 to 0.8 V. In the beginning, the surface layer is further lifted up slightly, and then the relaxation starts to occur. This change is not compatible with a simple



Figure 3: Vertical displacement of the surface atomic layer of the Pt(111) electrode in the methanol solution after the potential scan from 0.0 to 0.8 V [3].

model for CO desorption, which considers a decrease in the surface area of the CO layer during CO desorption, but can be explained by the formation of a more strongly adsorbed and less-dense CO layer. The CO layer would be tentatively formed by surface diffusion of CO during desorption, and suppression of repulsive CO-CO interaction in the less-dense layer results in the stronger CO-Pt interaction.

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T. Shirasawa^{1, 2}, T. Masuda³, W. Voegeli⁴, E. Arakawa⁴, C. Kamezawa⁴, T. Takahashi⁴, K. Uosaki³ and T. Matsushita⁵ (¹AIST, ²JST, PRESTO, ³NIMS, ⁴Tokyo Gakugei Univ., ⁵KEK-IMSS-PF)