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.

The high-speed technique was used to capture the atomic-scale phenomena at the electrochemical interfaces [2]. 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 real-time monitoring.

Figure 2 displays the 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].

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 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.

REFERENCES