Liquid Electrochemistry Explored by XPS and HAXPES

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X-ray photoelectron spectroscopy (XPS), which is capable of nondestructive analysis of the elemental composition, oxidation states, and chemical bonding of solid surfaces, is one of the indispensable techniques for current research and development. Since photoelectrons emitted by irradiation of x-rays are detected by an electron analyzer, a vacuum environment is required to avoid the scattering of photoelectrons in gas and liquid phases. However, tremendous efforts have been dedicated to the utilization of XPS for liquid and solid-liquid interfaces.[1-5]

In the 1970s, Siegbahn et al. performed a pioneering liquid measurement by using the "liquid jet" in which a liquid column generated from a liquid nozzle placed in a vacuum chamber can be measured by a differentially-pumped electron analyzer.[6] Thereafter, various innovative techniques for exploring the electrochemical interfaces have been developed. One is the utilization of "dip and pull" method; a thin liquid layer-coated electrode surface partially pulled up from a liquid reservoir placed in an analysis chamber can be measured by near ambient pressure (NAP-) XPS.

An alternative approach is the utilization of environmental cells; liquid is encapsulated in the environmental cell by using an ultrathin membrane as a separator between vacuum and ambient, and x-rays are incident on the membrane to detect photoelectrons generated from liquid, membrane and membrane/liquid interfaces (Fig. 1). If the membrane acts as a working electrode, electrochemical processes taking place at the solid/liquid interfaces can be observed.

Our group previously demonstrated an in situ XPS measurement of electrochemical processes at solid/liquid interfaces under the potential control using an environmental cell with a 15 nm-thick silicon membrane as a x-ray/photoelectron window.[7,8] In the study, electrochemical growth of Si oxide in contact with water was observed through the 15 nm-thick silicon membrane by using hard x-rays from a synchrotron light source. Recently, we further developed a laboratory-based XPS equipped with a conventional Al Kα source, and solution species encapsulated within the environmental cell were successfully observed. Here, we present our recent progress on "Liquid Electrochemistry Explored by XPS and HAXPES".

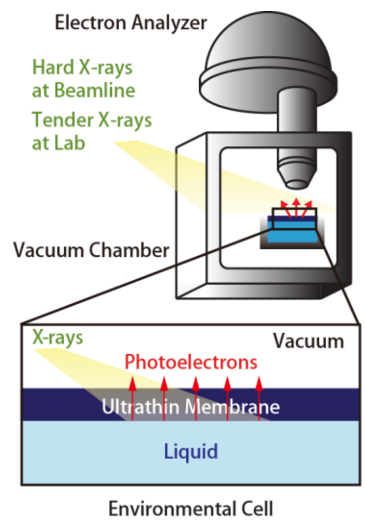

Fig. 1: Schematic drawing of XPS measurements of liquid and solid/liquid interfaces by using an environmental cell.

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