Electrochemical Surface Science ~Importance of Surface Imaging with Atomic Scale~

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Electrochemistry is an important field for industries concerned with products and processes such as batteries, fuel cells, solar cells, electroplating, corrosion prevention, electro-organic synthesis, and sensors. Because electrode reactions take place at the solid–liquid interface, where the electrode is in contact with an electrolyte solution, the electrochemical method can control the electron-transfer reaction by the applied potential. Until the early 1970s, various techniques such as Auger electron spectroscopy, X-ray photoelectron spectroscopy, surface X-ray scattering, and low-energy electron diffraction (LEED) were established surface-characterization tools. These methods can analyze elements and adlattices of thin layers on substrates; therefore, they were widely recognized as general analytical methods. However, these techniques are not *in situ* but rather *ex situ* methods because the sample is usually transferred into an ultrahigh vacuum environment (UHV).

We and other groups have constructed the so-called electrochemical STM (EC-STM) with the four-electrode configuration in 1988, in which the electrochemical potentials of the working and the tip electrodes can be simultaneously controlled with respect to a reference electrode. This EC-STM led to its valuation as arguably the premier technique for atomic level investigations of electrochemical reactions. It is well-known that high-resolution STM allows one to directly determine packing arrangements and even the structures of organic molecules adsorbed at electrode–electrolyte interfaces. *In situ* STM also allows one to monitor various electrode processes, such as the adsorption of inorganic and organic species and underpotential deposition (UPD) at atomic resolution.

The development of the EC-STM technique established the field of electrochemical surface science. *In situ* STM and AFM allows us not only to determine interfacial structures but also to follow electrochemical reactions. In contrast to investigations of the solid–liquid interface, recent advances in STM have improved our understanding of characteristic molecular assemblies and allow for the construction of nano-architectures. STM is a powerful tool for molecular-level analyses and characterization not only in electrochemistry but also in coordination chemistry and supramolecular chemistry. It is certain that these new methods will continue to be the premier techniques in various fundamental and related industrial processes taking place at solid–liquid interface.

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