Discovering New Electrochemical Avenues from Fundamental Research

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Until 1980, there had been only few in situ methods available for structural determination of an electrode surface in solution at a nanometer scale, scanning tunneling microscopy (STM) invented by Binnig and Rohrer in ultra-high-vacuum (UHV) in 1981. Belatedly, but assuredly, developments in STM operated at electrode surfaces in solutions allowed us to observe atoms and molecules at electrode surfaces, for the first time. This in situ STM raised the level of other techniques such as atomic force microscopy (AFM), infrared reflection absorption spectroscopy (IRAS) and surface-enhanced infrared reflection absorption spectroscopy (SEIRAS), second harmonic generation (SHG), sum frequency generation (SFG), and surface X-ray scattering (SXS) for in situ characterization of electrode surfaces under potential control with atomic and molecular resolution.

The other important progresses in the electrochemical surface science is the method to expose well-defined and clean electrode surfaces in aqueous electrolyte solutions without the use of ultrahigh vacuum (UHV) techniques developed by Clavilier, the so-called flame annealing and quenching method, which demonstrated by the fact that the adsorption-desorption reaction of hydrogen on clean Pt single crystal electrodes is strongly dependent on their crystallographic orientations; this demonstrated the importance of the nature (structure and cleanness) of metal surfaces at the atomic level. It cannot be overemphasized that evaluation of true electrochemical reactions should be started with clean surfaces even for polycrystalline without contaminations and oxides. These undesired materials existed on the electrode surfaces greatly affect following reactions. Particularly, the electro- and electro-less deposition of metals needs strong attention on this matter. The other important caution is the purity of solutions. We found many cases that small amount of contaminations such as halides and others which are strongly adsorbed on electrode surfaces and resulted in completely different reactions.

Thus, the establishment of both the preparation of well-defined clean electrode surfaces and in situ characterization techniques make it possible to monitor with atomic and/or molecular levels for not only electrode processes including under-potential deposition (UPD) and bulk depositions of metal ions, specifically-adsorbed anions, formation and characterization of self-assembled monolayer (SAMs) of organothiols, supramolecularly-assembled molecular adlayers and so on.

A recent advance in in-situ surface characterization techniques makes it possible to understand of electrolyte-electrode interface at atomic and molecular levels. The use of those in-situ techniques established in the past decade and the results have provided much knowledge for various electrode reaction processes including batteries, fuel cells and new surface design.

In the near future, the electrochemical surface science will be a very important subject for many industrial processes and devices for the control of various electrochemical reaction taking place on electrode surfaces with an atomic scale.