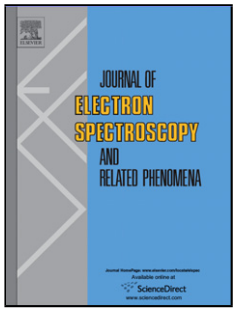

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In situ determination of electronic structure at solid/liquid interfaces

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ABSTRACT: Various important processes take place at solid/liquid interfaces. Understanding of structural changes accompanying with those interfacial processes is important not only for fundamental science but also for a wide range of applications, especially electrocatalysis. In the last several decades, a variety of microscopic and spectroscopic techniques have been developed to observe geometric/molecular/electronic structures at the solid/liquid interfaces in situ. However, techniques to probe the electronic structure of electrocatalysts are still limited because of the complexity of the experimental setup and the interpretation of results. Since the 1980s, our groups have developed and utilized various techniques which enable to investigate those structural changes under electrochemical potential control. In the present paper, our recent research progress on the electronic structure at solid/liquid interfaces, (1) in situ XAFS studies on molecular catalysts confined within molecular layers and electrocatalysts for oxygen reduction reaction in polymer electrolyte membrane fuel cells, (2) development of an in situ electrochemical XPS apparatus for the solid/liquid interfaces and (3) investigation of the electronic structure of metal surfaces modulated by adsorbed species by in situ DR-SFG are briefly reviewed.

Introduction.

Multi-electron transfer reactions at solid/liquid interfaces have been of a great interest in relation to the energy conversion devices such as fuel cells, water electrolysis and photocatalysts. Various important steps including mass/electron transfer, adsorption/desorption, oxidation/reduction, deposition/dissolution and formation/cleavage of chemical bonds take place during the multi-electron transfer reactions. Understanding of those interrelated steps is important not only for fundamental science but also for rational synthesis of highly efficient and/or durable electrocatalysts because they have a significant impact on the entire reaction efficiency.

In the last several decades, a variety of microscopic and spectroscopic techniques for surface analysis have been developed in conjunction with advances in optics, electronics, and quantum beams, and soon utilized for in situ observation of the structural changes induced by those interfacial processes.[1,2] For example, geometric structure of single crystal metal surfaces in contact with electrolyte solutions, including adsorbed species, has been determined at an atomic resolution by scanning probe microscopy (SPM)[3-13] and surface x-ray scattering (SXS).[14-23] Molecular structure of the adsorbed species at various solid/liquid interfaces has been identified by infrared reflection absorption spectroscopy (IRAS),[24-29] surface-enhanced Raman spectroscopy (SERS), sum frequency generation spectroscopy (SFG),[30-32] and X-ray absorption fine structure (XAFS).[33-36] In recent years, even the surface analysis techniques using electrons as a probe, which intrinsically require vacuum, such as scanning/transmission electron microscopy (SEM/TEM)[37-40] and x-ray photoelectron spectroscopy (XPS)[41] have been utilized to observe the electrochemical processes at solid/liquid interfaces.

However, in situ techniques to probe the electronic structure of electrode surfaces are still limited although it plays crucial roles in multi-electron transfer reactions.[42-44] For example, second harmonic generation (SHG) spectroscopy is capable of characterizing the electronic structure of surfaces, but it has yet to be widely used because of the complexity of the experimental setup and the interpretation of results. X-ray and electron spectroscopies can also determine the electronic state of the materials but they are often restricted by machine time and/or re-