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### Microtopography of Electrochemical Surface Layers

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## MICROTOPOGRAPHY OF ELECTROCHEMICAL SURFACE LAYERS

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The microtopography of surfaces resulting from the electrochemical transformation of surface layers is of interest in electrochemical energy storage and many other applications. The topography is also indicative of the structure of the underlying material and the mechanism of the surface transformation reaction.

Experimental observations of the microtopography of electrochemical surface layers have been made by previously-used spectroscopic ellipsometry and newly-developed elastic light scattering, Raman spectroscopy, and scanning tunneling microscopy in combination with electrochemical measurements and several ex situ techniques for surface analysis (eg. SEM, AES, XRD). In situ techniques are preferred because rapid changes in surface topography have been observed to occur at open circuit.

Spectroscopic ellipsometry is used to determine spectral properties of surface materials and to derive wavelength-independent parameters pertaining to film structure. Measurements at different wavelengths serve as independent monochromatic input, and film parameters are derived by the optimization of multidimensional optical models. By minimizing the difference between measurements and model predictions, spectral variations in film optical properties (generally time independent) as well as changes in film thicknesses and structure (time dependent) can be obtained. Raman spectroscopy of surface layers for chemical characterization is conducted with equipment sensitive enough to observe unenhanced emission. This high sensitivity is achieved by using a multilayer optical filter for removing the scattered incident wavelength, a single monochromator to disperse the light, and a multichannel plate detector for observing the entire spectrum simultaneously. In situ angularly-resolved elastic light scattering has been conducted by collecting scattered light over the angles of  $5-85^\circ$  from the incident direction in  $1^\circ$  increments with fiber optic probes. Elastic light scattering has been used to measure changes in the spectral power density function (SPDF) of the surface during anodic oxidation. The integral of the SPDF is a measure of the RMS roughness of the surface, and the angular dependence of the SPDF is related to the size of the growing particles. Scanning tunneling microscopy is used to provide surface topography with atomic-level spacial resolution. Surface profiles have been numerically converted to differential gray images and analyzed to derive amplitude density and autocorrelation functions.

Light scattering measurements and scanning tunneling microscopy have confirmed earlier conclusions from ellipsometer observations on the redistribution of silver oxide during the early stages of anodic film formation in alkali. Initially, a compact film grows via a diffusion controlled process. Later, three-dimensional nuclei form, and act as diffusion sinks for a dissolved silver species. A large number of small nuclei is transformed to a lesser number of large crystals during this redistribution by the action of the dissolved silver species.

The oxidation and reduction of a Cu (111) surface in KOH has been determined by spectroscopic ellipsometry to involve a compact cuprous oxide ( $Cu_2O$ ) layer. The anodic film grows according to a parabolic growth law under potential step conditions, indicative of diffusion-controlled growth by an active species in the film. However, the thickness of the film is only half of that expected on the basis of a charge analysis, indicating a loss due to a soluble material. Film formation and reduction during a potential sweep experiment shows that complete reduction of the film occurs, corresponding to the observed current response. Raman spectroscopy has shown that the onset of  $Cu_2O$  and  $Cu(OH)_2$  formation occurs at the first and second current peaks of the anodic potential sweep. In the oxygen evolution region, indications of a trivalent copper compound have been observed. Light scattering measurements show very small ( $200 \text{ \AA}$ ) surface features for  $Cu_2O$ , in agreement the ellipsometric measurements. During the later  $Cu(OH)_2$  formation, the surface roughness continues to increase as needles of about  $600 \text{ \AA}$  diameter are formed. SEM photographs have been used to confirm this observations.

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