Dynamic Stress Analysis at Solid Electrodes

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Monitoring the curvature of a cantilever in solution and under potential control is a well established method for studying the stress developing at the electrode-electrolyte interface. These in situ stress measurements have already provided insight into a range of electrochemical processes such as underpotential deposition, adsorption of anions, hydrogen electroinsertion, electrodeposition, etc… In dynamic stress analysis (DSA) the responses of both the current (as in electrochemical impedance spectroscopy) and the stress to an oscillating input voltage are measured simultaneously. By changing the frequency of the input signal, electrochemical processes with different characteristic time constants can be separated.

DSA has been applied to determine the fundamental relationship between the surface stress (f) and the charge density (q) for both Au and Pt cantilever electrodes immersed in 0.1 M $HClO_4$. For both metals, a direct relationship between f and q was found over a wide range of frequencies and potentials. Figure 1 shows that the phase angle of the surface stress with respect to the charge for the Pt cantilever varies greatly with the dc potential: in the double layer region f and q are 180 degrees out of phase while in the hydrogen region they are in phase (i.e. a negative charge induces compressive stress). A zero degree phase angle is also observed for capacitive charging of the oxide-covered surface. For Au, no such transition was observed, with the surface stress always 180 degrees out of phase with the charge density.

DSA was also applied to gain insight into the post coalescence stress developing during the electrochemical growth of copper films. Copper was deposited on an Au cantilever from a 0.1 M H_2SO_4 electrolyte with controlled amount of $CuSO_4$. DSA measurements were started after the copper thickness reached about 200 nm. DSA for frequencies between 20 Hz (to avoid the resonant frequency of the cantilever which is close to 40 Hz) and 0.1 Hz is then performed. A clear frequency dependence of both the amplitude and the phase of the stress response has been observed when the mass transport was not diffusion limited. Specifically the amplitude of the stress-thickness begins to increase for frequencies below 1 Hz. These results are consistent with the idea that, driven by differences in chemical potential between the surface and the grain boundaries, the copper adatoms can diffuse in and out of the grain boundaries.

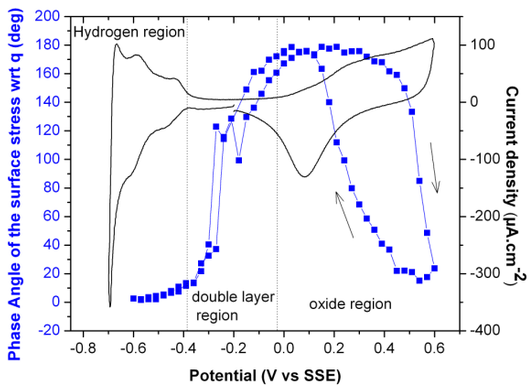

Figure 1. Cyclic voltammetry and variation of the phase angle of the stress response to a 50 mV input perturbation for a Pt cantilever in 0.1 M $HClO_4$.