Nanoscale Images and Dynamics of Ag Dissolution and Dealloying using Coherent X-rays

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New nanoscale insights were obtained into electrochemical dissolution phenomena in Ag crystals using coherent x-ray scattering techniques. First, an atomically smooth silver single crystal surface was studied to investigate step dynamics1 using coherent surface x-ray diffraction. We measured the applied potential dependent rate of atomic step motion of the Ag(001) surface in weak NaF electrolyte using x-ray photon correlation spectroscopy (XPCS). The step motion occurs because of the dissolution-redeposition dynamics at the step edges. For applied potentials between hydrogen evolution and oxidation, the surface configuration completely changes on timescales of 10–104 seconds depending upon the applied potential (Fig. 1). The potential dependence was modeled with the step line capacitance.

Based on the dynamics we learned from the single crystal surfaces, we studied silver nanoparticle dissolution during electrochemically-driven dissolution reactions.2 A silver nanoparticle was stepped to a dissolution potential in 0.1 M HClO4 solution and imaged with Bragg coherent diffraction imaging (BCDI) (Fig. 2). A series of images of the silver particle suggest that the dissolution reaction occurs in two distinctive steps. There is an incubation period with no apparent dissolution occurs until a partial dislocation loop, with two ends terminating on the nanoparticle surface, is created. Once the dislocation loop is exposed to the electrolyte, a rapid preferential dissolution follows. In the third example, we imaged dealloying, or the selective dissolution of the less-noble species, processes of Ag from both Ag-Au alloy nanocrystals and thin-film grains.3 Significant differences in the structures and morphologies were found between the nanocrystals and nanograins during and after dealloying. In particular, dealloyed nanoparticles exhibited an increase in strain relative to their as-synthesized state while dealloyed grains exhibited similar strains to their as-synthesized state. All three topics will be presented in the context of electrochemical reaction phenomena and some implications of the results will be discussed.


Fig. 1. XPCS results of Ag(001) surface. Decay constant (τ) as a function of applied potential at L=0.2. The solid black line corresponds to only the contribution from step line capacitance, while the red line includes the phenomenological component. For reference, PZC is near −0.8 V where the surface and line capacitances are zero.

Fig. 2. BCDI of a silver nanoparticle. Dissolution proceeds in two steps: i) creation of dislocations and ii) rapid dissolution at or near the dislocation loop exposed to the acidic electrolyte. (a-b) The particle shape and size does not change during the initial 30 sec in the dissolution overpotential of 0.25 V. (c-d) Significant dissolution occurs after the appearance of a dislocation loop (60 sec) exposed to the electrolyte. (e) Eventual increase of Ag concentration in electrolyte slows further dissolution of the particle (120 sec).

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