

Electrochemical AFM with rod-like samples: Cu deposition on a commercial Pt electrode

Application Note AN00964

A unique feature of the Nanosurf Electrochemistry Stage ECS 204 is the capability to handle both flat and rod-like samples for simultaneous AFM and electrochemical measurements. This capability is exemplified here by an *in situ* electrochemical AFM experiment showing copper electrodeposition and stripping on a commercial rod-like platinum electrode.

Electrodeposition of metals on conductive supports is a fundamentally and technologically important class of electrochemical reactions. In this experiment we electrochemically deposited copper on a commercial rod-like platinum working electrode (CHI102, CH Instruments, \varnothing 2 mm). The platinum is embedded in insulating Kel-F sheath (\varnothing 6.35 mm). The Pt electrode was mounted in a cylindrical sample holder that was then fixed in ECS 204 (Figure 1). As a reference electrode we employed commercial Ag/AgCl/3.4 M KCl electrode (ET072, eDAQ). A platinum wire acted as a counter electrode. After mounting, 1.5 ml of 1 mM CuSO_4 and 50 mM H_2SO_4 aqueous solution were added into the liquid cell. An AFM probe of type NCSTAuD (Nanosensors) was installed into a liquid-compatible cantilever holder and used in dynamic imaging mode. The ECS 204 stage was placed on an active vibration isolation table during all experiments.

Figure 2 shows cyclic voltammograms of the Pt electrode during the EC-AFM experiment. A single positive-going peak at $E \approx 0.16$ V against Ag/AgCl is observed on CV measured in potential range $-0.2 < E < 0.3$ V (black curve). A second anodic peak developed at $E \approx 0.03$ V when the lower return potential was decreased to -0.25 and -0.3 V (green and red curves). This second peak is attributed to the oxidative dissolution of metallic copper that was deposited on Pt surface at $E < -0.2$ V.

To obtain small copper clusters on Pt surface, we performed a single potential sweep at 50 mV/s to the lower limit $E = -0.4$ V, and subsequently stopped the sweep at $E = -0.05$ V during the return scan. The latter potential corresponds to a (quasi)equilibrium between Cu clusters on Pt surface and Cu^{2+} ions in solution, where the clusters neither dissolve, nor grow further. An AFM image of Cu clusters on Pt surface is shown in Figure 3. While acquiring Figure 3, the electrode potential was first kept in equilibrium at $E = -0.05$ V (upper part of image). After the upper half of Figure 3 was recorded, the potential was scanned to $E = 0.3$ V with the sweep rate at 50 mV/s at the position of the green horizontal line. This leads to a quick dissolution of Cu clusters. The lower part of Figure 3 shows Pt surface free of Cu clusters.

This *in situ* electrochemical AFM experiment with a commercial electrode is applicable to a wide range of other rod-like samples. The Electrochemistry Stage ECS 204 enables simultaneous electrochemical and AFM characterization of their surfaces under environmental control.

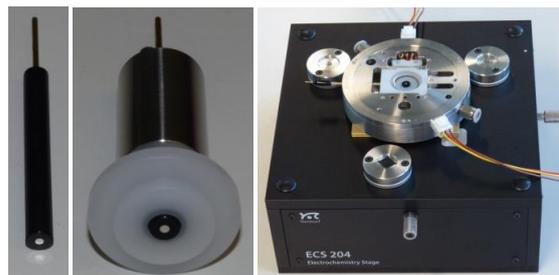


Figure 1. Rod-like electrode (left) mounted inside a sample holder (center) and fixed in Electrochemistry Stage ECS 204 (right).

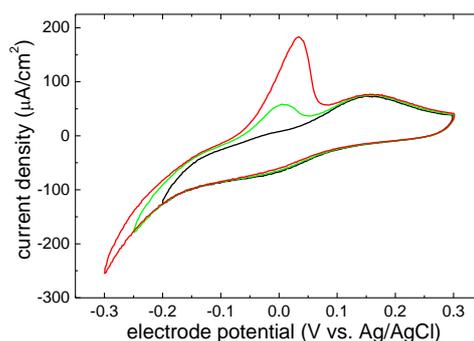


Figure 2. Steady-state cyclic voltammograms of Pt electrode mounted in ECS 204 measured in 1 mM CuSO_4 + 50 mM H_2SO_4 with the sweep rate 50 mV/s. Current density was calculated using geometric area of the electrode.

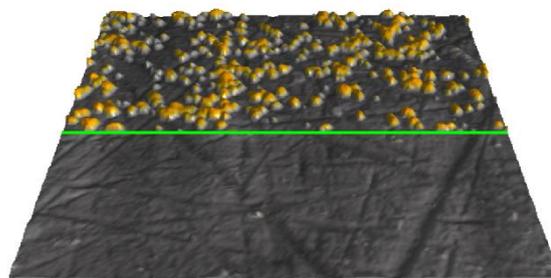


Figure 3. *In situ* AFM image in 1 mM CuSO_4 + 50 mM H_2SO_4 showing Pt surface covered with electrochemically deposited copper clusters at $E = -0.05$ V (upper part) and bare Pt surface at $E = 0.3$ V (lower part), $3 \mu\text{m} \times 3 \mu\text{m}$, vertical range 100 nm. The potential scan was performed at the position of the horizontal green line.