

Oxygen-free EC-AFM experiments with Electrochemistry Stage ECS 204

Application Note AN00952

Ambient oxygen is known to readily dissolve in aqueous solutions and produce a reduction wave that interferes with many electrode reactions. Therefore, it is common to employ oxygen-free solutions for electrochemical experiments. In electrochemical SPM experiments, the deoxygenation represents a major technical challenge, and the studies are often limited to reactions which are not or only slightly affected by the presence of oxygen in solution. In this application note we describe how to carry out electrochemical AFM experiments in oxygen-free aqueous solutions employing FlexAFM and Electrochemistry Stage ECS 204 from Nanosurf.

In this experiment we identified the presence or absence of dissolved oxygen empirically, by the presence or absence of oxygen reduction wave. As an AFM sample and working electrode we employed commercial rod-like working electrode (CHI104, CH Instruments, \varnothing 3mm) made from glassy carbon (GC) embedded in insulating Kel-F sheath. Using such inert material as GC allowed us to observe oxygen reduction wave in a wide potential range. Furthermore, we used aqueous 0.1 M NaOH as electrolyte to suppress hydrogen evolution at negative potentials.

The GC electrode was mounted in ECS 204 (Figure 1). As a reference electrode we employed a commercial Ag/AgCl/3.4 M KCl electrode (ET072, eDAQ). Platinum wire acted as a counter electrode. After mounting, 1.5 ml of 0.1 M NaOH solution was added into the EC-AFM cell. The ECS 204 stage was located on a vibration damping table during all experiments.

The steady-state cyclic voltammogram measured in the open cell in as-prepared solution (that was therefore saturated by ambient oxygen) is shown by red line in Figure 2. Further an AFM probe of the type NCSTAuD (Nanosensors) was installed into a cantilever holder suitable for AFM measurements in liquid; the holder was mounted on the FlexAFM scan head and the FlexAFM scan head was placed onto ECS 204. A sealing membrane was attached to the FlexAFM scan head (Figure 3).

When the FlexAFM scan head is placed onto ECS 204, the sealing membrane attaches to magnets located on the top of ECS 204. This creates a small volume protected from the ambient around the electrochemical cell and the cantilever holder. Gas tubes were then attached to gas inlet and outlet (Figure 1). To avoid a backflow of the ambient air, the free side of the outlet tube was immersed into a beaker with water. The gas tightness of the setup was considered to be satisfactory when a small gas flow at the inlet was sufficient to observe gas bubbling through water at the outlet.

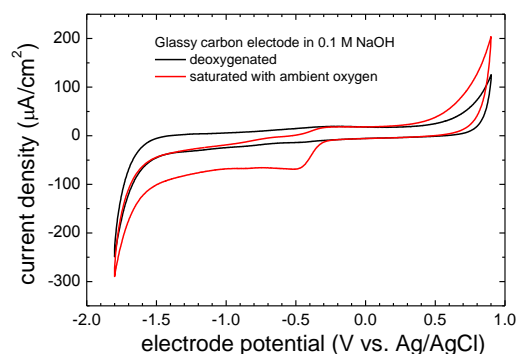


Figure 2. Steady-state cyclic voltammograms of glassy carbon electrode mounted in Electrochemistry Stage ECS 204 as measured in 0.1 M NaOH with the sweep rate 50 mV/s: (red) in open cell with as-prepared solution and (black) in deoxygenated solution. Current density was calculated using geometric area of the electrode.

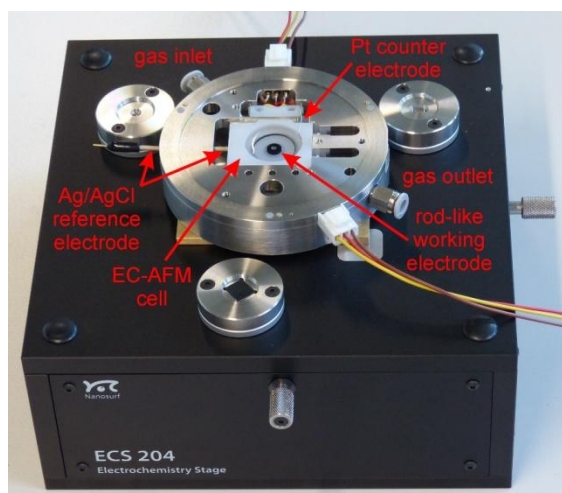


Figure 1. ECS 204 with mounted rod-like electrode.



Figure 3. Photo of FlexAFM scan head with a sealing membrane.

Figure 4 shows an image of cantilever immersed in solution as observed through the FlexAFM camera (side view) after the laser alignment. One clearly sees a laser spot on the end of the cantilever (above) and its reflection in the electrode (below). Using lateral translation mechanism integrated into ECS 204, the AFM probe was positioned above the GC surface, which is seen as a lighter circle in the middle surrounded by a darker Kel-F sheath.

To remove oxygen from the solution, we purged nitrogen through the protected volume above the solution. In order to replace air in the protected volume, we first used a strong gas flow for 15 minutes. Once the atmosphere above the solution contains no oxygen, the rate of oxygen removal from the solution is determined by its diffusion in aqueous phase and is not affected by the gas flow rate. Therefore, after 15 minutes of purging we reduced the gas flow rate to a minimum value sufficient to create bubbles at the outlet. Cyclic voltammograms were continuously recorded during the deoxygenation. After approximately 2 hours, they converged to a stable shape that did not change during next 10 min. Comparison of this voltammogram (black line in Figure 2), one recorded before deoxygenation (red line in Figure 2) and intermediate ones allows attribution of the reduction wave reaching maximum at ca. -0.5 V to the oxygen reduction. This wave is completely absent in the last voltammogram, which led us to conclusion that in this case the oxygen was completely removed from solution or, more strictly, its amount felt below the electrochemically detectable level.

We stress that 2 hours needed to completely remove oxygen from as-prepared solution represent rather an upper estimate of the deoxygenation time. It can be significantly reduced if one adds an already deoxygenated solution into the cell.

Once the deoxygenation was finished, we approached the AFM probe to the sample and imaged the sample in dynamic mode.

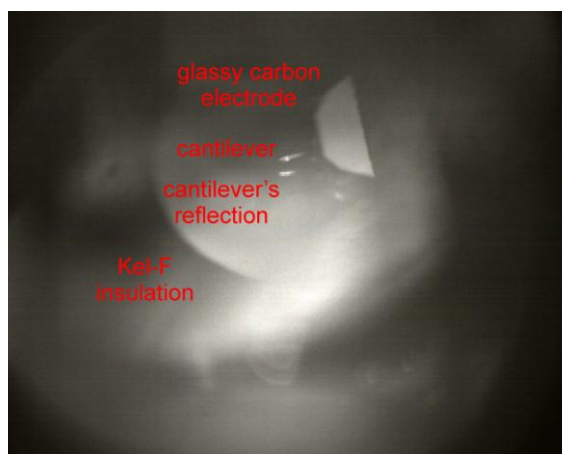


Figure 4. Optical image of AFM cantilever above GC electrode as observed through the FlexAFM camera (side view).

We found that it is possible to perform stable AFM imaging while there is a gas overpressure at the inlet, but only if there were no bubbles at the outlet. It means that in this case the gas was dissipated through unavoidable small holes. If the overpressure was high enough to produce bubbles at the outlet, we observed periodic spikes on AFM images, which frequency correlated with the gas flow and bubbling rates. We attribute these artifacts to vibration of the outlet tube and/or pressure shock waves inside the gas that occur during the bubble release.

Figure 5 shows image of bare GC surface obtained in 0.1 M NaOH under potential control. It shows a grained surface interrupted by long lines created during the polishing of the electrode. Using the “Calculate Area Roughness” tool of Nanosurf software, we calculated from the image in Figure 5 a root mean square roughness of 11.9 nm.

Our results indicate feasibility of oxygen-free in situ AFM imaging experiments in Electrochemistry Stage ECS 204. Commercially available rod-like electrodes similar to the one employed in this work can be mounted in ECS 204 stage and simultaneously characterized electrochemically employing professional third-party equipment and by AFM (imaging and spectroscopy) using Nanosurf FlexAFM. Combined in situ structural, nanomechanical and electrochemical studies may be employed to address various surface processes such as electrodeposition of different materials or corrosion. Furthermore, electrodes of this type can also serve as substrates for the assembly of active materials (organic layers, nanoparticles, biomolecules, cells), which structure, mechanical properties and electrocatalytic activity can be characterized simultaneously in an electrochemical AFM experiment.

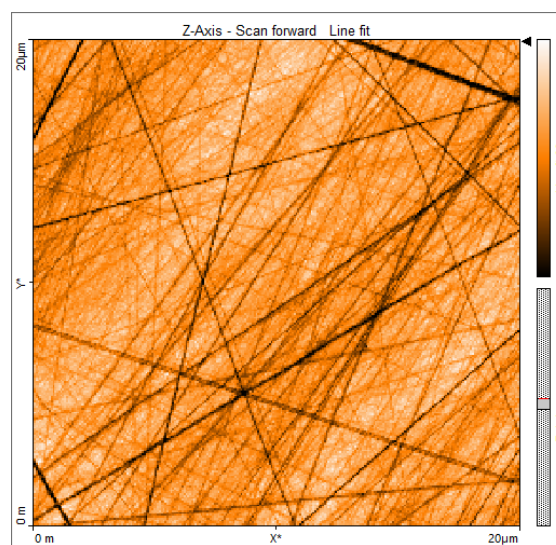


Figure 5. AFM image of GC surface (topography with “Line fit” filter) obtained in 0.1 M NaOH under potential control.