



Tunneling spectroscopy of clean and adsorbate-covered gold surfaces in humid air, measured with fast bias voltage ramps



Raphael Rösch*, Rolf Schuster*

Institute of Physical Chemistry, Karlsruhe Institute of Technology, 76131 Karlsruhe, Germany

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ABSTRACT

The noise level of tunneling spectroscopic data can be significantly reduced by averaging the tunneling current over a large number of short bias voltage ramps, instead of recording over a single slow ramp. This effect is demonstrated for tunneling spectra of Au(111) by averaging over 200 consecutive bias voltage ramps, each 500 μ s long. We attribute the improvement of the data quality to the frequency dependence of the current noise spectral density. Due to mechanical vibrations and tip instabilities the noise density is usually much higher for low frequencies ca. <1 kHz than for the high frequencies relevant for measuring with fast bias ramps. The high data quality allowed for the routine detection of the Au(111) surface state and the investigation of the influence of steps in humid air, i.e., with a water-covered tunneling gap. For a CN covered Au surface in the presence of water we unexpectedly found additional electronic density of states at positive energies, around 0.6 eV, i.e., for unoccupied states. STS spectra of a $(\sqrt{3} \times \sqrt{3})R30^\circ$ Cu-UPD layer, formed by adsorbed sulfate and Cu species, indicate tunneling via the sulfate electronic density of states.

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1. Introduction

The structure and composition of the liquid–solid interface formed between an electrolyte solution and an electrode are of great importance for the understanding of the fundamental processes of electrochemical reactions. However, the detailed analysis of the interface is challenging. Particularly for in-situ investigations in the presence of an electrolyte solution, only part of the well-established vacuum surface science techniques are applicable. Whereas structural information of the interface can still be obtained, e.g. by X-ray diffraction, IR spectroscopy or in-situ scanning tunneling microscopy (see e.g. refs. [1–4]), methods for the in-situ study of the electronic structure of the interface are hardly available.

Scanning Tunneling Spectroscopy (STS) is one of the few methods, which could provide in-situ information about the local electronic structure of the interface. As pointed out e.g. in ref. [5–11] the dependence of the tunneling current on the tunneling voltage between the tunneling tip and the sample reflects the local electronic density of states (LDOS) of the surface. STS is in principle directly applicable to electrochemical systems. For example Halbritter et al. studied the interface of the Ag-surface in perchloric acid [12]. Tunneling spectroscopy was very successfully employed for the in-situ, local determination of the band gap of semiconducting surface layers like Zn–Sb deposits in ionic liquids

[13] and self-assembled monolayers in trimethylbenzene [14]. Space charge effects and semiconducting properties were studied by STS on passivating films in aqueous electrolytes [15,16]. Hugelmann and Schindler presented a careful study on the general feasibility of voltage tunneling spectroscopy on Au(111) surfaces in perchloric acid electrolytes and the influence of oxygen on the spectra [17]. In electrochemical systems beside the tunneling voltage between tip and surface also the potential of the sample and the tip vs. the reference electrode can be varied in parallel, keeping the tunneling voltage constant. Wandlowski and coworkers intensively studied the charge transfer between surface and tip via redox-active molecules by this method [18,19]. Similarly Tao studied the apparent height of porphyrin molecules at an Au surface, dependent on their oxidation state [20].

The mentioned studies impressively demonstrate the potential of STS also in electrochemical environment. However, more subtle features of the surface electronic density of states, like e.g. the surface state of an Au(111) surface, as almost routinely observed in vacuum systems [21–28] are hitherto inaccessible in electrochemical systems. To our knowledge the observation of the Au(111) surface state outside UHV environment was so far limited to the study by Hulsken et al., who observed the Au(111) surface state in tetradecane [29] and a study by Kowalczyk et al. who observed signatures of the Au surface state on a contaminated Au sample in air [30]. The Au(111) surface state typically leads to a variation of the tunneling current by only a few percent. For the determination of the electronic density of states the derivative of the tunneling current with respect to the tunneling voltage has to be formed. Thus, detecting the Au surface state requires

* Corresponding authors.

E-mail addresses: raphael.roesch@asu.edu (R. Rösch), rolf.schuster@kit.edu (R. Schuster).

high stability and low noise measurements of the tunneling current, which are obviously more difficult to achieve in electrochemical environment than in vacuum studies. Beside mechanical instabilities there are reasons intrinsic to the electrochemical environment like additional noise due to adsorbate molecules and substrate adatoms diffusing through the tunneling gap or frequent variations of the tip geometry in electrochemical environment. Very often such noise sources are located in the low frequency range typically below a few kHz. For example, typical low-lying and easy to excite mechanical resonance frequencies of single tube piezos are of the order of 1 kHz. The noise found in STM images of Au-surfaces in 0.1 M HClO₄ upon lifting the reconstruction indicates the diffusion of Au adatoms, crossing the tunneling gap on millisecond timescale [31]. Often occasional ‘jumps’ of the tunneling tip, i.e., tip instabilities occur on the time scale of seconds to milliseconds. Thus in typical tunneling experiments the noise density at low frequencies is substantially higher than above a few kHz.

In the current contribution we reduce the influence of low frequency noise on the recorded tunneling current–voltage curves by the application of fast, typically only 500 μs long voltage ramps, followed by appropriate averaging. Our experiments are conducted in humid air, which is expected to lead to the formation of a water meniscus with a diameter up to hundreds of nanometers between the hydrophilic Au surface and the tip [32]. Therefore, tunneling spectroscopy experiments in humid air could be considered as model system for in-situ electrochemical STS investigations in a miniature electrochemical cell with negligible leakage currents, however lacking control of the electrolyte potential. We first verify the benefits of our experimental approach by comparing tunneling current measurements with fast and slow voltage ramps. Then we present STS data on the Au(111) surface state on water covered surfaces, on a cyanide layer on Au(111) as well as on an underpotentially deposited Cu layer, which was ex-situ investigated.

2. Experimental

Tunneling experiments were conducted in a home-built electrochemical STM open to air, similar to the one described e.g. in [33]. The tunneling current was measured via a home-built high speed current–voltage converter based on an OPA 657 (Texas Instruments) operational amplifier, which achieved a –3 dB limiting frequency above 700 kHz. For recording the tunneling spectra the current signal was digitized by a National Instrument PCI-6251 card. The control of the voltage ramps as well as data evaluation was performed using IgorPro (Wavemetrics). Typically the tunneling current was recorded with a time resolution of 1 data point/μs. The recording of one STS data set lasted for 110 ms and started with the deactivation of the STM feedback circuit. During the first 10 ms the tunneling current was recorded at constant tunneling voltage to check the stability of the tunneling gap. This was followed by the application of 200 triangular bias ramps with duration of 500 μs each. After recording the STS data the STM feedback loop was reactivated. For experiments with a single, slow voltage ramp the 200 voltage ramps were substituted by a single 100 ms long ramp. Before further processing, the collected data was preselected by picking only experiments where all consecutive 200 ramps were completely recorded. Typically more than 90% of the recorded data sets pass this selection criterion. The current signals of the individual ramps were averaged and then slightly smoothed with a sliding average of ±10 points. The chosen smoothing procedure is similar to the application of a 50 kHz low pass filter. Finally, the normalized differential tunneling conductance (dI/dU) / (I/U) was calculated by numerical differentiation of the smoothed data. The normalized differential tunneling conductance was introduced by Strosio et al. [9] to account for the exponential dependence of the tunneling current on tip surface separation and on tunneling voltage. It provides a relatively direct measure of the electronic density of states (DOS). The bias voltages indicated in the following spectra represent the potential of the sample. Therefore negative

bias voltage corresponds to DOS of the sample below the Fermi energy, i.e., to filled electronic states of the sample.

The relative humidity was checked before every experiment and was between 60 and 90% which is sufficient to guarantee a thin water layer on the gold substrate [32].

Au samples were prepared by thermal evaporation of 200 nm of gold on freshly cleaved mica substrates under high-vacuum conditions. Before the STM experiments the samples were flame-annealed with a Bunsen burner, which led to extended (111) oriented terraces. STM tips were cut from gold wire ($\varnothing = 0.25$ mm, 99.999%) with a cutter.

For cyanide adsorption on Au the method described by Murray and Bodroff [34] was used. 10 ml of ultrapure water, 35 mg of KCN and the annealed gold film were placed in a sealed beaker for 72 h. The Au surface did not touch the cyanide solution and the adsorption proceeds via the air. Samples treated that way showed superstructures in STM images, indicative of the formation of ordered CN adlayers, as discussed below.

Copper was deposited on the Au films in a small electrochemical cell from 10 mM H₂SO₄ + 200 μM CuSO₄ solution. A copper wire was used as reference and a platinum plate as counter electrode. The electrochemical behavior and the purity of the system were checked by cyclic voltammetry. Before emersion of the sample the potential was adjusted ca. 100 mV positive of the potential of the copper bulk deposition to form an underpotentially deposited ordered ($\sqrt{3} \times \sqrt{3}$)R30° Cu overlayer (Cu UPD), containing 2/3 monolayer (ML) Cu and 1/3 ML sulfate-ions [1,35–37]. The samples were emersed from the electrolyte under potential control to keep the deposited monolayer including the electrochemical double layer intact [38]. Afterwards the samples were transferred into the STM setup without further treatment. STM images indeed revealed a $\sqrt{3} \times \sqrt{3}$ structure on the surface (inset in Fig. 5), indicating that the Cu UPD layer remained on the surface. In addition after performing the STS experiments, up to 60 min after the original emersion, the sample could be reimmersed into the electrolyte and the Cu UPD layer could be electrochemically dissolved.

3. Results and discussion

3.1. Comparison between averaged fast and single slow voltage ramps

Fig. 1a shows the resulting tunneling current transient of a conventional STS experiment, conducted with a single tunneling voltage ramp on Au(111) with an Au tip. Before ramping the bias voltage, the tunneling conditions were $U_T = 10$ mV and $I_T = 1$ nA. At $t = 0$ the bias voltage started to increase from 10 mV to 1 V within 50 ms. Afterwards the voltage was ramped back to 10 mV. The current signal is symmetric, i.e., forward and backward scans exhibit the same current–voltage characteristic. However, the signal appears quite noisy, particularly at high currents, i.e., high tunneling voltages. We attribute the current fluctuations to essentially two sources, i) tip instabilities, where the geometry of the tip is instantaneously changing by diffusion or by electromigration of the atoms in the high field of the tip–surface gap, similar to the origin of current fluctuations in nanocontacts [39–42], and ii) to electrochemical reactions in the thin water layer between tip and surface, e.g., oxidation of the gold surface and the accompanying enhanced adatom diffusion [43,44]. The current transient of 100 ms duration consists of 500 data points of which each data point represents the average current value of a 200 μs long time intervals. Considering the Nyquist theorem, which states that the sampling frequency (in this case: 1 data point per 200 μs) is about twice the maximum measurable frequency, this corresponds to an upper cut off frequency of the current measurement of about $1/(2 \cdot 200 \mu\text{s}) = 2.5$ kHz.

In Fig. 1b the averaged current transient of 200 consecutive 500 μs long ramps is shown. The total recording time for the fast ramps was thus $200 \cdot 500 \mu\text{s} = 100$ ms which is identical to the total duration of the slow ramp. The data set was recorded subsequently to the data of Fig. 1a in the same experiment without noticeable changes of the tip.

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