

In situ monitoring of electrochemical reactions using SPR Navi 200

Introduction

In some cases multiple detection techniques are required to understand surface phenomena and interactions, or external stimuli is needed to initiate certain reactions. Electrochemistry is well suited to be paired with the surface plasmon resonance (SPR) because both are surface probing techniques. The SPR can provide real time information of surface changes and the sensor surface can be used as working electrode for electrochemistry at the same time. The electrochemical setup can then be used as an additional parallel measurement technique, or a source of stimuli for electrochemical reactions.

The parallel measurement can be used for example characterizing organic, inorganic or hybrid conductor and insulator materials and monitoring deposition of such materials. With the parallel measurements it is also possible to detect trace metals with high precision in solution.

Materials and methods

In this experiment copper was electrodeposited on gold by cyclic voltammetry from 0.01 M CuSO_4 solution with 0.1 M H_2SO_4 as carrier electrolyte.

BioNavis SPR Navi 200 equipped with an electrochemical flow cell accessory was used for the measurements (Fig.1). The electrochemical cell had the SPR sensor gold surface as working electrode and 0.5 mm platinum wire as both counter and reference electrodes. The electrodes are easily exchangeable, and also other electrodes such as Ag/AgCl can be used when appropriate.

The cyclic voltammetry was performed from 0.0 to 0.6 V and started always from the equilibrium potential present at the time in the cell. Three experiments were performed: angular scan (AS) and fixed angle experiments (FA) both using potential scan rate of 0.005 V/s and performing three cycles, and a FA experiment using 0.1 V/s potential scan and twenty cycles.

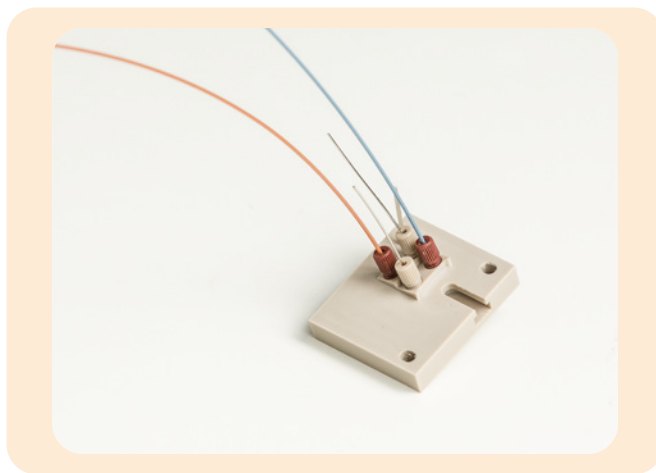


Figure 1. An electro-chemical flow cell of SPR Navi 200.

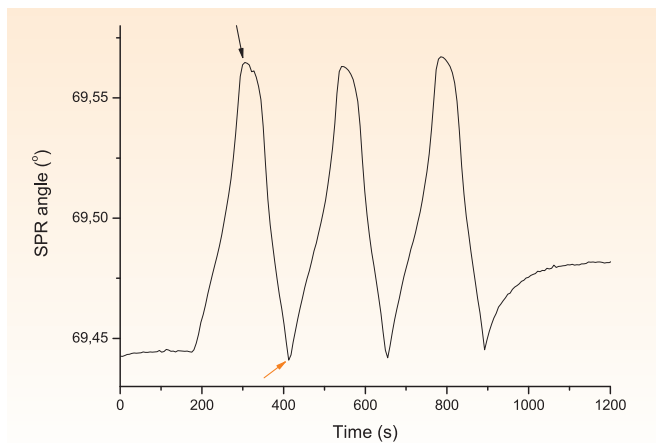


Figure 2. Angular scan peak minimum sensogram of the electrochemical measurement.

Results and discussion

The measured sensograms are presented in Figures 2 (AS) and 3 (both FA). Cyclic voltametry current versus potential graphs for both scan rates are presented in Figure4. Full SPR curve scans corresponding to the "minimum" and "maximum" as marked on the sensogram in Figure2 are presented in Figure5.

It can be seen from the Figure2 that the slower potential scanning AS experiment is in equilibrium, because the maxima and minima positions do not change between cycles. Also it is clear from the Figure3 that the fast potential scanning does not allow the system to reach equilibrium in between scans and the deposition is clearly changing over cycle number. Also as the potential scanning is faster, the current created by the reaction is order of magnitude bigger than in than with the slower scanning (Figure4). This is because the reaction takes place much faster, which results in a higher electron flow and therefore higher current.

The amount of deposited copper can be accurately estimated by using Winspall [1] and fitting the two SPR scans presented in Figure5 to solve the layer thickness. The fitting procedure uses shape change of the whole SPR peak created by the new layer and takes into account the complex refractive index of the material. This method is especially useful for materials which have higher absorption coefficient (k), but also higher real part of the refractive index (n) than gold, like copper does. Material of this kind actually produces negative and non-linear SPR minimum shift with increasing adlayer thickness. Traditional SPR analysis, where the peak position or intensity change is evaluated, can give misleading results in such cases. It is also interesting to note that the deposited copper ad-layer is actually sharpening the SPR peak (decreasing its half-width). The half-width parameter can be also monitored in real-time by the SPR Navi 200. The copper ad-layer deposited during the 0.005 V/s scan rate was calculated to correspond to 1 nm thick uniform copper layer, corresponding approximately to 900 ng/cm² of deposited mass.

Conclusions

The electrochemical cell module can add a simultaneous parallel measurement method or a stimuli system for the BioNavis SPR Navi 200. Measuring in parallel the same sample in the same cell increases the accuracy of such measurements as compared to separate measurements, as it is certain that exactly the same conditions are used in both measurements. The ability of measuring the full angular range and a full SPR-curve benefit greatly in applications with metals and other highly absorbing materials, which give non-linear SPR response.

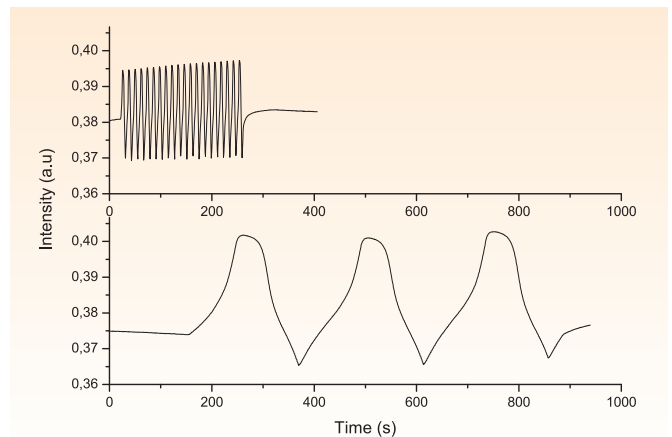


Figure 3. Fixed angle sensograms of the electrochemical measurements using two different potential scan rates.

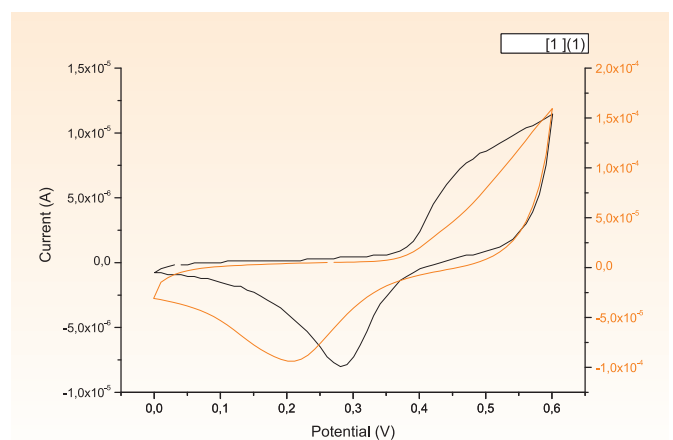


Figure 4. Cyclic voltametry scans for slow scanning (black) and fast scanning (orange).

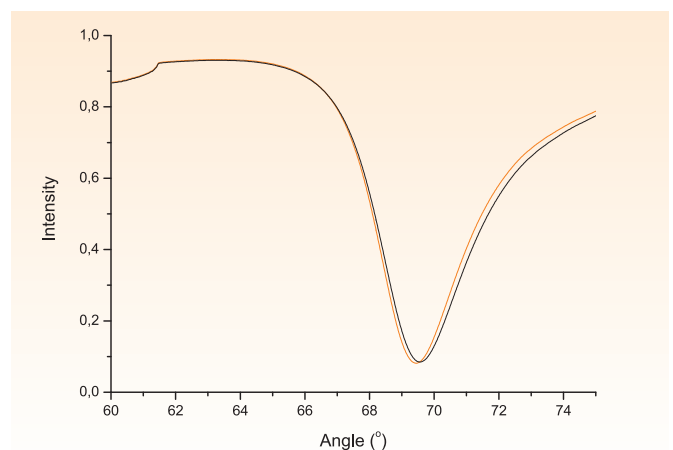


Figure 5. The SPR peaks corresponding to the arrows marked in Figure2.

[1] Winspall software: <http://www.mpip-mainz.mpg.de/knoll/soft/index.html>