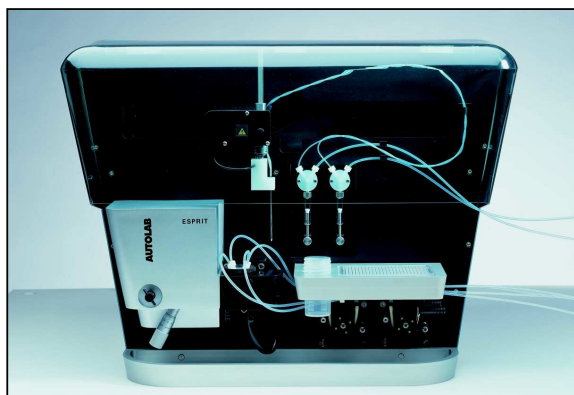


## AUTOLAB APPLICATION NOTE



### ESPR Measurements on conducting polymers: electropolymerization of aniline

Conducting polymers are of great importance for applications in electrochromic displays, batteries and sensors. As there are many factors that influence the oxidation and reduction (or doping/dedoping) of these polymers, retrieving information from electrochemistry alone is quite difficult and it is therefore useful to combine electrochemistry with in-situ techniques as for example QCM, FTIR, or AFM. In this application note, the results will be shown of combined electrochemistry and surface plasmon resonance

measurements on the electropolymerization of aniline, a widely used system for electrode modification.

### Experimental

All experiments have been done with an Autolab ESPRIT system in combination with an Autolab PGSTAT30 potentiostat. A picture of the cuvette that is used for the combined electrochemistry and SPR measurements is shown below.



The ESPRIT system is a double channel SPR instrument, with the possibility to combine electrochemistry and SPR. The system has two channels so that one channel is used for reference measurements. In case the system is used for E(llectrochemical)SPR, electrochemistry is done in one channel only.

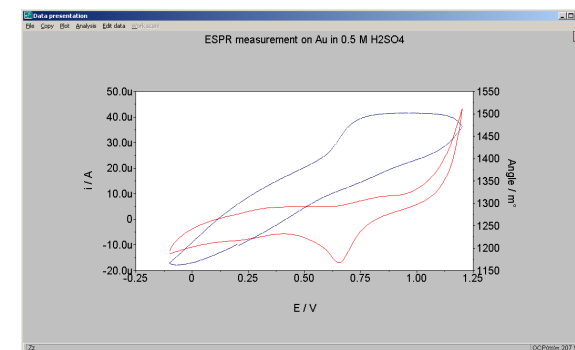
Aniline was electropolymerised on the gold SPR disk surface from a solution containing 0.1 M aniline and 0.5 M H<sub>2</sub>SO<sub>4</sub>. A solid Ag/AgCl

electrode was used as a reference, a Pt rod as a counter electrode.

### Results

#### ESPR on Au in 0.5 M H<sub>2</sub>SO<sub>4</sub>

In the figure below a cyclic voltammogram (red) is shown of Au in 0.5 M H<sub>2</sub>SO<sub>4</sub> during which the SPR signal (blue) was measured simultaneously.



The oxidation of the Au surface (above 0.7 V) and the reduction of that oxide (peak at ca. 0.7 V) are clearly visible. In the SPR signal the formation and the reduction of the oxide are also clearly visible.

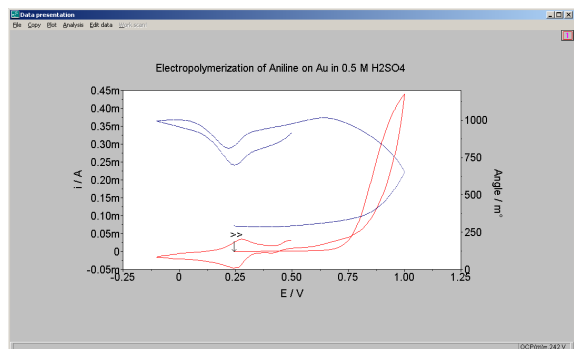
#### ESPR of electropolymerization of Aniline

Polyaniline was made on the Au surface by applying a potential sweep between -0.1 Volt and 1 Volt with 100 mV/s. The result is shown in the curve below.

From the start potential (which was chosen at OCP and is indicated in the graph by the arrows), the potential is scanned in positive direction. The large increase in current at potentials above 0.75

## AUTOLAB APPLICATION NOTE

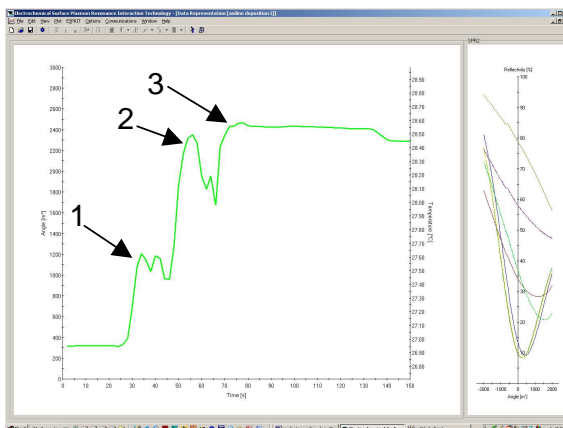
Volt is in the literature<sup>1</sup> ascribed to the oxidation of



the aniline monomer to form the aniline dimer which is a precursor for the polyaniline. With those strong oxidation currents one can clearly see a strong increase in angle (blue) as well indicating that the product that is formed adsorbs on the Au surface. The polyaniline layer keeps growing (as can be seen in the angle change) also in the backwards scan until 0.5 Volt. In the lower potential range (0.25 Volt) a redox couple is visible, which is ascribed to electron transfer from and to the already formed polyaniline layer. The changes in angle that are visible in this potential range are ascribed to doping and dedoping of the polymer layer with anions (in this case sulphate) from solution<sup>1,2</sup>.

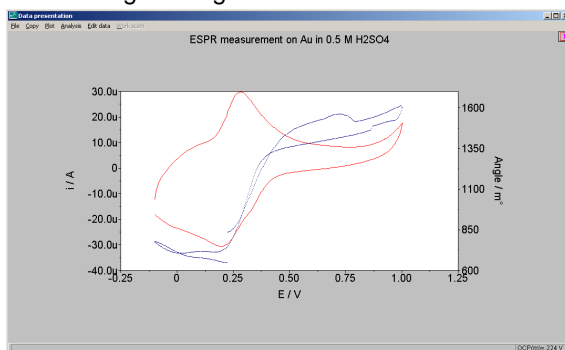
The figure below shows the change in SPR angle as measured with the ESPRIT software, one can clearly see that the increase in SPR angle is continuous and at the limit of the instrument very fast (after three cycles). The numbers in the graph are the scan numbers. The fact that already at 3 cycles the angle limit is reached means that the

refractive index change upon polyaniline formation is high.



### ESPR of polyaniline in 0.5 M H<sub>2</sub>SO<sub>4</sub>

After electrodeposition the cuvette was flushed with 0.5 M H<sub>2</sub>SO<sub>4</sub> to be able to measure only the adsorbed polyaniline. The resulting Cyclic Voltammogram is given below.



The electron transfer from and to the polyaniline is clearly visible (redox couple at 0.25 Volt), whereas in the SPR signal (blue) one can clearly see the effect of anion (sulfate) desorption (increasing angle) and adsorption (decreasing angle).

<sup>1</sup> A.Baba et al. J. Electroanal. Chem. **562**, 95-103 (2004)

<sup>2</sup> S. Mu et al. Synth. Met. **123**, 249 (1997)