Preparation of SERS active electrodes via electrocrystallization of silver

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Because of ecological concerns, the classic ‘wet’ photography has been recently replaced by thermally developable imaging systems (TDPM). Like in the classical photographic systems, a visible image is formed by the reduction of a silver ion source, in this case a silver carboxylate. This reaction generates the metallic silver particles forming the visible image. The reaction is induced by heat, and not by chemicals like in the classical case.

Further developments of this technique are hindered by the lack of knowledge about the silver reduction reaction. No fundamental research about this is found in literature. The global reaction consists of different steps (complexation reactions, mass transfer, charge transfer,…) which are unknown at this moment and need to be investigated.

A TDPM contains various components to achieve the desired properties for today’s demanding applications. Indications exist that adsorption of these additives on the growing silver image plays a major role.

These adsorption phenomena as well as their influence on the above-mentioned processes should be thoroughly studied.

A spectro-electrochemical method is worked out to investigate the influence of additives on the reduction of a metal carboxylate.

Several techniques can contribute to the unravelment of the mechanism of the silver carboxylate reduction. Linear sweep voltammetry combined with a rotating disc electrode is used to gain insight in mass and charge transfer. The adsorption of components will be studied with Raman spectroscopy, which is, thanks to the ‘Surface Enhanced Raman Scattering’ effect, very much suited for this purpose.

In this paper the choice and the preparation of the working electrode, on which the study will be performed, is discussed.

For the electrochemical investigation, we showed previously (1 and refs cited herein) that the pretreatment of the electrode is a crucial step in creating stationary conditions for the measurements. Also the SERS study requires a specific electrode pretreatment (2). Here roughness is the determining parameter. Moreover, the surface chemistry has a strong influence on the adsorption behaviour. Especially the presence of sulphur and chlorine components is to be avoided.

In a first step the electrode material is selected.Two possible candidates are proposed: a silver or a platinum electrode. The advantage of a platinum electrode is that the yield of the silver reduction reaction can be determined by re-oxidation of the deposited silver. This is impossible on a silver electrode, since in this case the electrode itself will be oxidized.

A silver electrode has the advantage that the situation is more comparable to what is happening during development in a TDPM, namely growth of the silver nuclei by further deposition of silver. The study of the silver deposition on a silver electrode is representative for this phase of the development.

These considerations lead to the choice to work with a platinum electrode on which silver is pre-deposited in a precisely controlled manner. This way, the advantages of both electrode materials are combined: the reduction is studied on a surface covered with silver particles which simulates the development and since one knows the amount of silver which is pre-deposited, the yield of the reduction can be calculated by a re-oxidation of all the deposited silver.

An additional advantage of this choice is that, by giving the pre-deposit a certain roughness, SERS-spectra of adsorbed molecules can be obtained on this electrode. This permits to study adsorption phenomena as well as the silver reduction reaction on the same surface. Since all occurring processes are intimately coupled, studying them on the same substrate is of great importance.

Secondly, an appropriate electrolyte and deposition technique are chosen. The purest surface chemistry is obtained by depositing silver from a $AgNO_3$ solution. As deposition technique a double potential step is chosen. The parameters are the applied overpotential, the silver nitrate concentration and the deposition time. The corresponding chronoamperometric data is used to optimize the resulting silver deposit morphology.

A variety of combinations of the selected parameters was tested, leading to the choice of the optimal pre-plating conditions (3).

A SEM-micrograph of a deposit obtained via this procedure is given in Fig 1, together with the corresponding SERS-spectrum of 10^{-4}M 1-phenyl-5-mercaptotetrazole (PMT). The electrolyte contains 0.5M $LiNO_3$ and 5 10^{-4}M $AgNO_3$. For the first step a potential difference of 0.22V is imposed during 2s, for the next step 0.32V during 10s is selected. The chronoamperometric transient to produce this deposit is also shown in Fig. 1.

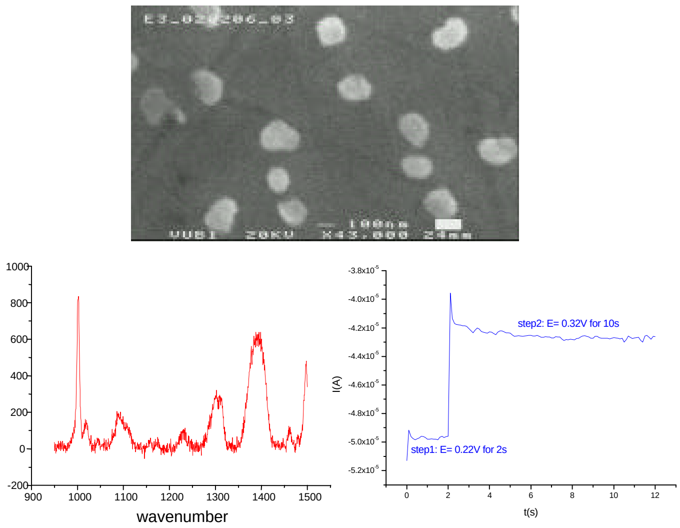

Fig 1: SEM-micrograph of an electrode roughened via a double potential step. The corresponding chronoamperometric transients and the SERS spectrum of 10^{-4}M PMT are also shown.

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