Simple Fabrication of a Silver Epoxy Coated Microelectrode for SECM Imaging in Small Volumes

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During the last twenty years advances in electronics and computing have allowed the development of microelectrodes [1] that are suitable for analytical measurements in a reduced space. The microelectrode has relevant applications in biology to study the chemistry of species released by a single cell, in materials to study corrosion process (e.g. pitting corrosion), or in chemistry to study the kinetics of charge transfer between interfaces. The microelectrode can be used alone or integrated in the scanning electrochemical microscope (SECM), first described by Bard´s group [2, 3] in the 80s. In a conventional SECM experiment, the sample to be analyzed is immersed in a solution containing electroactive species, which acts as a mediator for the measurement. Preparation of a sample for imaging frequently includes sectioning of the sample and mounting in a matrix of resin epoxy. After that the sample is placed in cell which contains the solution and three electrodes: the SECM tip electrode, reference, and auxiliary electrodes. It is obvious that the volume of the cell must be sufficiently to contain all the elements mentioned.

An area of active interest in SECM is the study of localized corrosion. There are various literature reports of studies on pitting corrosion with the SECM. [4-8] In all cases the imaging with the SECM was done immersing the complete sample in the solution. However, due to nature of the phenomenon of pitting corrosion the use of just a small drop of solution could be very helpful to position the microelectrode in the restricted area around a pit and to get information from there, improving the understanding of this process.

Miniaturization of the electrochemical cell has been the subject of various reports in the literature. Spaine and Baur [9] have reported a miniaturized electrochemical cell assembled in theta capillaries. The cell was formed by a working electrode and a reference electrode, each one in each section of the theta capillary. With this assembly measurements in drops with volume around some picoliter can be achieved. However, fabrication of this micro-cell is not easy and requires expertise. Another experiment with the SECM in small volumes was reported by Turcu et al. [10] The authors describe the fabrication of a robust microelectrode coated with a coaxial silver layer. A ring of silver around the glass that insulates a Pt-disk is built and acts as a quasi-reference electrode. This first step in the preparation of the miniaturized probe was to fabricate the microelectrode and then an additional chemical deposition process was needed to build the silver coating.

We report an easy and simple fabrication process to make a microelectrode coated with epoxy containing silver particles (i.e. silver epoxy) which is proposed for electrochemistry and SECM in small volumes. In this sensor the coating acts as a quasi-reference electrode in the same way as a separate silver-wire quasi-reference electrode. The performance of the electrode is tested using cyclic voltammetry and the SECM. A volume of 1 µl was used in the SECM to get images of a defined 25-µm-diameter Pt substrate and of an Al/SiCp composite surface. The results show that silver-epoxy can be used instead as a quasi-reference electrode in small volumes. These coated microelectrodes possess important advantages for SECM imaging in small volumes: they are robust, do not require an additional process during fabrication, and are reusable.

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