**Polyaniline/Metal-based Electrodes: Preparation and use as Anodes in Bioelectrochemical Systems**

Laura Mais, Michele Mascia\*, Simonetta Palmas, Elisabetta Usai, Annalisa Vacca

*Dipartimento di Ingegneria Meccanica Chimica e dei Materiali, Università degli Studi di Cagliari, Via Marengo 3, 09123 Cagliari, Italy*

*\*Corresponding author: michele.mascia@unica.it*

**Highlights**

* A suitable three-step procedure is tested to coat metal electrodes with polyaniline
* Uniform and stable films of polyaniline can be obtained
* High degree of surface coverage is measured
* The obtained electrodes can be used as bioanodes

**1. Introduction**

Carbon-based anodes have largely used in bio-electrochemical systems, due to their biocompatibility, chemical and microbial stability. However, carbon has a low electric conductivity, which may decrease the cell voltage and the efficiency of the system. Metals may be a suitable alternative, with high values of electrical conductivity, but few metals are stable in the potential window of bio-electrochemical systems and biocompatible.

Although Copper is known to be a natural antimicrobial material, active biofilms have been obtained on this metal [1]. Coating of metals with conductive and biocompatible polymers such as polyaniline (PANI) may prevent release of toxic ions and promote the biofilm growth. PANI have been proposed for different bioelectrochemical applications, such as electrochemical biosensors [2], cell adhesion [3] and tissue engineering [4].

In the present work, copper and gold substrates have been coated with the conductive polymer polyaniline, and tested for biofilm growth. The coating was obtained with a three-step procedure, proposed in a previous work with gold electrodes: the PANI film showed higher stability if compared with that obtained with simple elctropolymerisation of aniline on bare gold [5].

**2. Methods**

The experiments were carried out in a flow cell with planar electrodes (0.5 cm2); gold or copper were used as working electrode, platinum was used as counter electrode.

To obtain a stable and uniform coating of polymer, a three-step approach was followed: nitrophenyl group was grafted to the metal (Cu or Au) surface through electroreduction of nitrobenzendiazonium (NBD) salt in acetonitrile medium; the nitrogroup was then electrochemically reduced to amine in ethanol/water electrolyte; aniline was electropolymerized onto the surface of the amino-phenyl-modified electrodes. After each step, cyclic voltammetry and electrochemical impedance spectroscopy were used to characterize the modified surface.

The cells were then fed with anaerobic sludge and acetate, and the trend with time of the bioelectrocatalytic current of the acetate oxidation under potentiostatic conditions was monitored, as a measure of the biofilm growth onto the PANI/metal surface.

**3. Results and discussion**

Grafting of nitrophenyl groups onto metal surface was obtained in cyclic voltammetry: well-shaped peaks were observed in the first cathodic and attributed to the electroreduction of nitrobenzendiazonium. The reduction peak disappeared in the other scans, as the active sites of the metal surface were blocked by the organic moieties.

The surface coverage of the NBD modified electrodes was evaluated from the charge transfer resistance to electron transfer of the ferri/ferrocyanide redox probe by electrochemical impedance spectroscopy. Values of coating higher than 98% were obtained with gold electrodes, while lower values were observed with copper electrodes.

During the voltammetric reduction of nitro group to amine a cathodic peak was observed, which decreased with the number of cycles and disappeared after about ten cycles, indicating that all the electroactive grafted groups are reduced.

During electropolymerisation of aniline, well defined oxidation and reduction peaks were observed, indicating that the aminophenyl modified electrodes were effective for the self-catalytic head-to-tail polymerization of PANI. The peaks are less evident with copper electrodes. At the end of the process a uniform, well visible coating of PANI was obtained with both electrodes.

During biofilm cultivation under potentiostatic control with activated sludge and acetate, a growth of current can be observed, with an apparent lag phase.

**4. Conclusions**

Results show the effectiveness of the three-step procedure used for electrochemical coating of copper and gold with polyaniline. A stable and uniform coating of polyaniline was obtained with both metals.

Preliminary results on the use of PANi/metal electrodes as bioanodes are promising: the presence of PANI made possible to obtain an electrochemically active biofilm with copper electrodes.

**References**

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