



# Atomic force microscopy study of conducting polymer films near electrode's edge or grown on microband electrode



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## ABSTRACT

Polypyrrole (PPy) films of different thicknesses (within the range from 200 nm to 2.5  $\mu\text{m}$ ) were electrodeposited on two types of inhomogeneous substrates, single band and double-band Pt electrodes. Topographic images of the polymer layers were obtained by means of ex situ large-scale AFM technique to demonstrate how the propagation rates of the film growth above the electrode (in the normal direction to the electrode surface) and along the insulating surface surrounding the single- or double-band electrodes (in the horizontal direction) change with the deposition charge. It is proved that variations in the film thickness over the double band electrodes and progressive changes of the PPy morphology from compact thin film to rough thick layers represents an obstacle for reliable determination of the specific conductivity of the deposited polymer film from conductance/resistance data for such coated microband electrodes. Advantages and shortcomings of other methods of specific conductivity measurements of the polymer films are also discussed.

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## 1. Introduction

Surfaces of electrodes are frequently covered with a solid layer which may be composed of an oxide, salt, polymer, etc. Specific conductivity of the layer is one of its most important characteristics determining e.g. the ohmic potential drop across the film for a faradaic reaction taking place at the film/solution boundary. Experimental determination of this fundamental parameter of the material which forms a solid film on an insulating substrate or which represents a powder is usually carried out by means of the standard four-point/probe (van der Pauw) method [1,2] based on four "point" electrodes in contact with different points of the film (pressed between two insulating surfaces) so that two of them are used for passage of the current between them along the film while two others measure the induced potential difference

between them. The subsequent calculation of the specific conductivity is possible if the layer thickness is known while the layer is assumed to be uniform.

This technique cannot be used for a film in contact with electrode possessing a very high conductivity. Therefore, the layer has to be detached from its surface *without its damaging*. However, this procedure is practically impossible for very thin (well below the micrometer range) and well adhered films which is a typical situation for electrochemically deposited layers. Another disadvantage of this method is the necessity to grow the film on a relatively large electrode surface while it is much more difficult to ensure its uniformity at this scale. Besides, this method is inevitably ex situ, i.e. the film cannot be characterized under control of the electrode potential and in contact with electrolyte solution. This is a serious drawback since the conductivity of the same film frequently varies as a function of the electrode potential.

These problems of the above method are absent in another method of the conductivity measurement based on the electrochemical impedance spectroscopy [3,4] which is a powerful technique to study charge transport properties in various systems. However, determination of electrical parameters of the layer

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(including its specific conductivity) from experimental impedance data is crucially dependent on the choice of the physical model adequately describing the system under study and the calculation of the corresponding complex impedance. Such theoretical analysis has been carried out for numerous models (e.g. analytical formulas have been derived for a uniform layer with an electron-ion conductivity [5–7]) but thus obtained analytical or numerical results for the impedance contain frequently numerous unknown parameters of the system, to be determined from fitting to experimental data, which represents often a difficult task.

One should note that a dominant majority of these impedance theories considers a *one-dimensional* (1D) problem where all quantities depend only on a single spatial coordinate, e.g. the normal one for the current passage across a film. This approximation is substantiated by smallness of the film thickness compared to its horizontal extension and the uniformity of its local transport properties along the electrode surface. However, it is frequently left without attention that this description requires, strictly speaking, to ensuring also the 1D character of the charge transport inside the electrolyte solution. The latter corresponds to the configuration with two parallel large-surface-area planar electrodes (working and counter electrodes, WE and CE) separated by a thin solution layer. A similar 1D description (with minor modifications) is also applicable for systems with cylindrical and spherical symmetries.

Even though such configurations can be realized (and they are realized in some high-precision experiments) the dominant majority of impedance studies is carried out in conditions where the potential inside the solution is distributed in a 3D manner. Theoretical extension of the impedance theory to take this effect into account is not available as yet for electrodes covered with a conductive layer.

Because of these reasons the most largely used *in situ* method to measure the film resistance directly in contact with the electrode surface and for various oxidation levels of the film is based on the *microband* technique proposed by M. S. Wrighton et al. [8] and used later in several dozens of publications. In most cases it is a planar electrochemical setup which includes two closely-spaced electrodes separated by an insulating gap. They may represent two straight bands (see e.g. [9,10]), or possess a complicated shape (e.g. arrays) to increase their length (see e.g. [11–14]), i.e. the sensitivity. The widths of both bands and the gap fall in most cases into the interval from 5 to 200  $\mu\text{m}$ , or even larger.

The film for resistance measurements must cover this whole system including the insulating gap(s). For electrodeposited layers they are generated by imposing equal (or almost equal) potentials at both electrodes. The film grows initially up from their surfaces, covering progressively the insulating gap(s). Then, one can measure the current between two band electrodes via the coating, induced by a small-amplitude potential difference (which may be constant or alternating in time). Their ratio gives effective film conductance/resistance as a function of the average electrode potential, i.e. of the average oxidation level of the film.

A well-known drawback of this “two-electrode configuration” [14] is the current passage not only through the film covering the insulating gap but also across two electrode/film contacts. As a result, the measured resistance includes a contribution from the film and from these “contact resistances”. To separate these terms an analog of the 4-point method was realized within the microband technique [14]. Namely, each of the set of parallel planar band electrodes was connected electrically to one of the *four* external wires, two of them imposing slightly different potentials ensuring the desired oxidation level of the film and a current between these “current suppliers” while two other electrodes (located between the above mentioned electrodes) were kept at their open-circuit potentials (OCP), to register the potential difference between them. It is assumed that these systems, similar to “the 4-probe one”, provides

the values of the resistances along the film and across the electrode/film interface as functions of the basic electrode potential, i.e. of the oxidation level of the film.

The fundamental problem of the microband technique (both in its 2- and 4-electrode configurations) is an uncertainty with the “geometrical constant”,  $G_f$ , in the relation between the resistance of the film between its contacts with electrodes,  $R_f$ , and its specific conductivity,  $\kappa_f$ :  $R_f = G_f/\kappa_f$ . In some papers (see e.g. [9,10,12]) the geometrical constant was estimated assuming that the coating above the gap represented a *uniform layer* so that  $G_f = L_f/A_f$ , even though neither the numerical values of the “layer thickness”,  $L_f$ , and of the “cross-section area”,  $A_f$ , nor the way to find these values were not specified. This hypothesis of a “uniform layer” may not be considered as evident since the film grown from the electrode surface to cover finally the insulating gap *may have* a complicated shape both in the cross-section (perpendicular to the axis of gap) and along the gap.

To our best knowledge this shape has not been studied experimentally, at least for films of conjugated polymers while clarification of this point is of importance for the possibility to determine absolute values of the specific conductivity for such materials on the basis of measured data for  $R_f$ . In particular, it is of interest to verify the hypothesis that the film is propagating *along the insulating surface much faster* than it grows upward from the electrode surface.

Keeping this goal in mind we have carried out an experimental study of the process of the electroactive film growth over the surface of a microband electrode, in order to draw conclusions on the way to interpret resistance data for this system. Topographic images of the growing polymer layer were obtained by means of *ex situ* large-scale AFM technique which allowed us to trace the variation of the external profile of the deposited film on a *double-band* electrode surface depending on the deposition charge. Interpretation of these data is based on AFM imaging of similar films deposited on a *single-band* electrode, to demonstrate how the electroactive film is extending along the *adjacent insulating surface* in the course of the film growth.

The study was carried out for polypyrrole (PPy) as one of the most widely used electroactive/conjugated/electron-conducting polymer.

## 2. Experimental

Films of an electron-conducting polymer, polypyrrole (PPy), were grown electrochemically on planar electrodes which represented 300 nm-thick Pt layers lithographically coated on ceramic plates. Two different configurations (shown schematically in Fig. 1a and b, respectively) were used for these electrodes: (1) macrodisk (surface area: 0.38 mm<sup>2</sup>) connected with external circuit by a single band (width of about 8–10  $\mu\text{m}$ , see below); (2) double-band set (interdigitated configuration, widths of conducting bands and of insulating gaps between bands: about 5  $\mu\text{m}$ ).

Cleaning of the electrodes before polymer film deposition included steps of fast immersion into piranha solution, rinsing with water and keeping in acetonitrile (AN) under ultrasonic treatment for 5 minutes. Thus pretreated plate was placed in electrochemical cell containing deoxygenated acetonitrile solution of 1 mM pyrrole + 0.1 M TBAPF<sub>6</sub>. Polymer electrodeposition was carried out in conditions ensuring the maximal uniformity and flatness of the deposited film inside the internal areas of the electrodes [15] (as it is shown in Fig. 1c for the polymer layer on the macrodisk), in particular its minimal surface roughness, namely in potentiostatic regime at 0.7 V vs Ag/0.01 M Ag<sup>+</sup> in AN.

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