

# Influence of Incorporated Metal Particles on Switching of Polyaniline Films

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In contrast with the cyclic voltammograms, the ac impedance spectra of polyaniline films are shown to be strongly affected by the presence of relatively small amounts of Pt microparticles. The main effect observed is a large increase in the rate of redox switching of such doped films.

## 1. Introduction

One of the potentially important applications of electrically conducting polymer films is in their use as a matrix for electrochemical sensors. In such a context, polymer films frequently contain dispersed noble metal particles acting as electrocatalytically active sites for oxidation or reduction of the sensed substance. Dispersion of metallic (in general, platinum) microparticles inside conducting polymer (for example, polyaniline and polypyrrole) films may lead in some cases to a drastic modification of their electrochemical properties. This has recently been demonstrated as the absence of long-term poisoning during anodic oxidation of methanol at Pt/polypyrrole<sup>(1)</sup> and Pt/polyaniline<sup>(2)</sup> film electrodes. The corresponding electrodes were prepared by very slow cathodic deposition of platinum, at preformed conducting polymer films, resulting in a high dispersion of metal particles (most of the Pt particles were in the 2–10-nm-diameter range).<sup>(2)</sup> Such electrodes, used as anodes for the methanol oxidation at constant imposed potential, exhibited, in fact, stable (within few percent) currents over the 6 day period of the test. Earlier investigations have already demonstrated<sup>(3)</sup> that electrodeposition of small amounts of platinum into

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polyaniline films slow the decay of methanol oxidation currents with respect to a bulk Pt electrode. Besides affecting electrocatalytic activity of the conducting polymer films (which is a well-known effect<sup>(3-6)</sup>), dispersed metal microparticles also influence, to a large extent, their electrical properties.<sup>(7)</sup>

In the present study we describe a series of observations concerning changes in the conductivity behavior of polyaniline films induced by their modification with dispersed platinum microparticles. These findings shed light on the mechanism of charge transfer in polyaniline, which is a feature of considerable importance in view of the potential application of this polymer in electrochemical sensors and in electrochromic displays.

## 2. Experimental

The changes in conductivity of the films were monitored *in situ* by means of impedance measurements, which were carried out using a Solartron 1286 electrochemical interface and a Solartron 1260 frequency response analyzer controlled by a PCXT personal computer. The films of polyaniline were grown electrochemically on planar gold electrodes by continuously cycling, at  $50 \text{ mV s}^{-1}$ , the electrode potential between  $-0.18$  and  $0.745 \text{ V}$  vs the saturated calomel electrode [SCE]. Electropolymerization was carried out in  $2.2 \text{ M}$  solution of sulfuric acid containing  $0.5 \text{ M dm}^{-3}$  of freshly distilled aniline. In order to incorporate platinum microparticles into the polyaniline film, the electrodes were first soaked in a  $3.9 \times 10^{-3} \text{ M}$  solution of hexachloroplatinic acid in  $1 \text{ M H}_2\text{SO}_4$  for 20 min to enable anion exchange. Then the electrodes were rinsed with distilled water, transferred to  $1 \text{ M H}_2\text{SO}_4$  solution and cycled between  $-0.2$  and  $0.625 \text{ V}$ . Most of the electrochemical measurements were carried out at  $25^\circ\text{C}$  in  $1 \text{ M H}_2\text{SO}_4$  under a nitrogen atmosphere.

The final distribution of platinum on the surface as well as inside the polyaniline films was examined by scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX). The thickness of switched-off, dry polyaniline films was determined using an Alpha-step 200 profilometer (Tencor Instruments).

## 3. Results and Discussion

Figure 1 shows a typical cyclic voltammogram illustrating switching on (anodic) and off (cathodic) for  $45\text{-}\mu\text{m}$ -thick polyaniline film. The voltammogram is quasi reversible, with a visible charge hysteresis between the forward and reverse potential scans, and exhibits one oxidation and one reduction peak in the range of  $0 - 0.15 \text{ V}$ . The peak corresponding to the second oxidation reaction, was present in the range of  $0.7 - 0.8 \text{ V}$ , (not shown), but the sweep was usually not extended into this potential region to avoid the irreversible changes in physicochemical properties of the polyaniline film. The shape of the voltammogram in Fig. 1 remained practically unchanged even after incorporation of about  $100 \mu\text{g cm}^{-2}$  of Pt particles.

Impedance spectra of  $50\text{-}\mu\text{m}$ -thick polyaniline film switched on and off are shown in Figs. 2(a) and 2(b), respectively. The observed impedance plots are similar to those

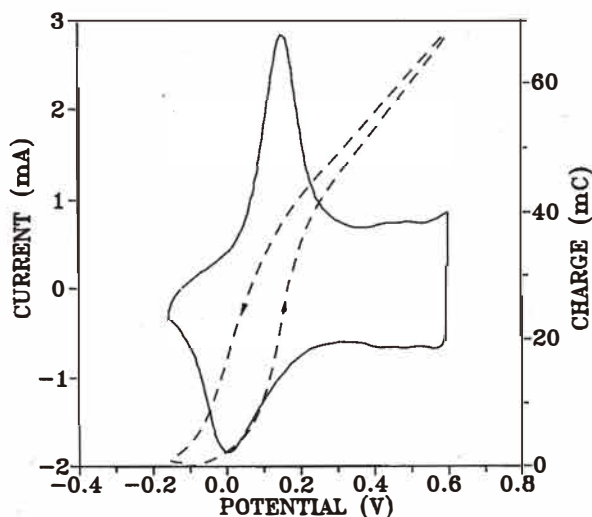


Fig. 1. Current-voltage profile recorded (at  $0.01 \text{ V s}^{-1}$ ) for a  $45\text{-}\mu\text{m}$ -thick polyaniline film in  $1 \text{ M H}_2\text{SO}_4$  (solid line). The dashed-line curves show amounts of charge involved in the oxidation (forward) and reduction (backward) scans.

obtained thus far in the case of thin polyaniline films.<sup>(8,9)</sup> The low-frequency regions of the plots are quite close to the vertical line corresponding to the response of a series RC element. The absence of a clearly discernible Warburg region in the low-frequency regions of the diagrams implies that the processes of ingress and egress of counterions, associated with the oxidation/reduction of the polymer film are not diffusion-controlled.

The reduction reaction of such a thick ( $50 \mu\text{m}$ ) polyaniline film proceeds, in fact, very slowly (cf. Fig. 3), and for some potentials it is not completed until after 5 – 6 h. These results are particularly relevant to the use of polyaniline films in chemiresistors, a kind of sensor responding to chemical species by a change of resistance between electrodes. For such devices, the response time should normally be in the range of seconds, the condition fulfilled by thin ( $< 1 \mu\text{m}$ ) polyaniline films, but not by the much thicker films, investigated in the present study. Thus, for the  $50\text{-}\mu\text{m}$ -thick polyaniline film, polarized at a potential of  $-0.1 \text{ V}$  at which, according to the voltammogram in Fig. 1, the film is in a switched-off state, a significant increase of both the real and imaginary parts of impedance is still observed after 30 min from the start of the reduction process (Fig. 3). Further increase of the thickness of the polyaniline films did not affect the overall shape of the impedance spectra; however, the rate at which the real and imaginary components attained their steady-state values became still slower. Especially notable is the very slow increase in the unmodified polyaniline-film resistance (Fig. 4 curve A) which accompanies the transition through the potential region corresponding to the process of switching off of the polymer (such a slow switching rate cannot be inferred from the shape of cyclic voltammograms).

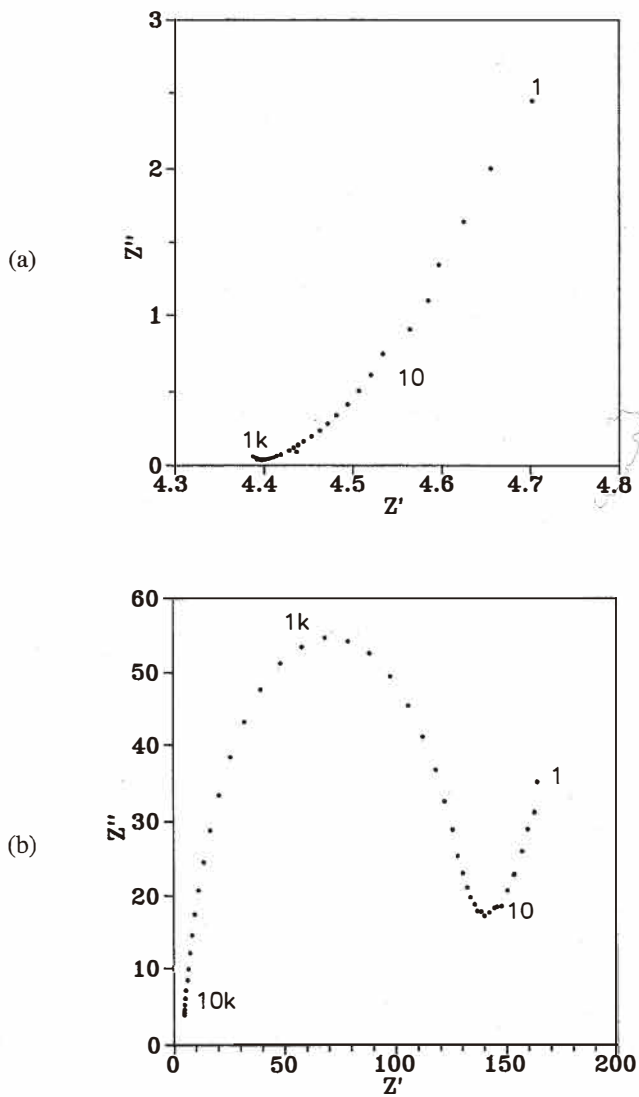


Fig. 2. Impedance spectra of a 50- $\mu\text{m}$ -thick polyaniline film (without Pt) in (a) a switched-on (at 0.5V vs SCE), and (b) a switched-off (at -0.1V) state.

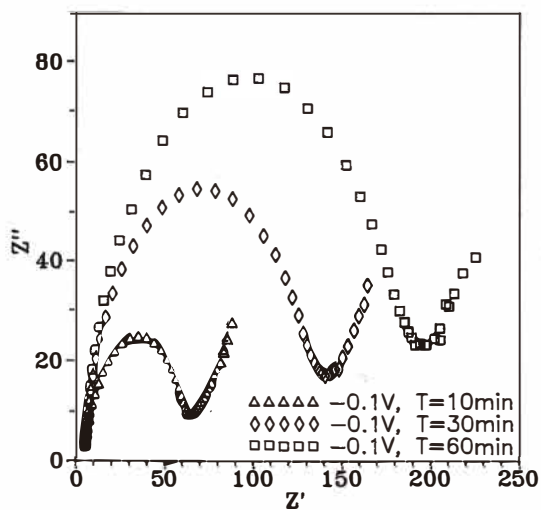


Fig. 3. Impedance spectra for the electrode from Fig. 2(b) measured at different times from the start of the polarization at  $-0.1$  V.

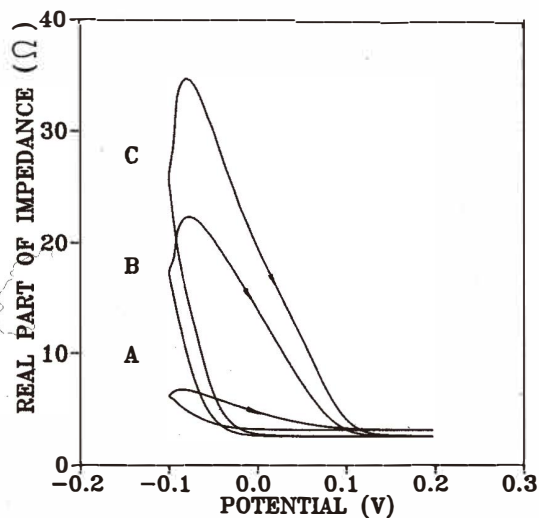


Fig. 4. Changes in the real part of impedance of a  $40\text{-}\mu\text{m}$ -thick polyaniline film without platinum (curve A) and after the incorporation of  $70 \mu\text{g cm}^{-2}$  of Pt (curve B) and of  $200 \mu\text{g cm}^{-2}$  of Pt (curve C). Scan rate is  $0.01\text{V s}^{-1}$ .

The model frequently used to describe the switching of polyaniline films assumes the rate of mass transport of ionic species in and out of the film to be the rate-determining step. However, such a model cannot explain the long-term variation of the impedance components. On the other hand, slow conformational changes (involving in some cases relaxation times ranging from minutes to hours) have been shown to accompany charging/discharging processes in conducting polymers, such as, polythiophene.<sup>(10)</sup> It is, however, not clear whether a direct connection can be established between the occurrence of the geometrical relaxation and the slow changes in the impedance spectra observed in the present study. It should be recalled, in this connection, that the thick films of polyaniline are known to be structurally inhomogeneous. For example, the inner (about 100-nm-thick) layer of the polymer film, located near the electrode support, remains much denser than the outer layer. These structural inhomogeneities appear to be the most plausible reason for the existence of poorly conducting regions in nominally oxidized polyaniline films, on the one hand, and for still well conducting regions in the films reduced within the voltammetric time scale, on the other.

The incorporation of less than  $100 \mu\text{g cm}^{-2}$  of Pt particles into 40 – 50- $\mu\text{m}$ -thick polyaniline films results in a strong enhancement of the rate of redox switching. Figure 4 illustrates the effect of Pt doping on the variation of impedance of the polyaniline electrode as a function of the potential. The switching became much more rapid for the polymer with about  $70 \mu\text{g cm}^{-2}$  of dispersed metal microparticles (curve B). Interestingly, a subsequent significant increase of the amount of incorporated platinum caused only a slight change in the polyaniline switching rate. A SEM micrograph (not shown) of the electrode in the case of Fig. 4, curve B, exhibited a network of polyaniline fibrils partly covered with Pt particles and aggregates of different sizes. Most of them were spherical and about 50 nm in diameter. The Pt to C ratio (from EDX) in a cross section of the polyaniline film was almost constant (there was some accumulation of platinum at the film/solution interface), indicating a reasonably uniform distribution of the metal inside the polymer film.

The presence of platinum microparticles distributed along the polymer fibrils is thought to facilitate the hopping of charge carriers between adjacent polymer chain segments and through poorly conducting regions of the polyaniline film. Such an explanation is in good agreement with previously proposed models,<sup>(11–13)</sup> according to which the ohmic resistance of the film and/or the electron transfer at an expanding boundary between conducting and nonconducting regions are the rate-determining factors in the redox switching.

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