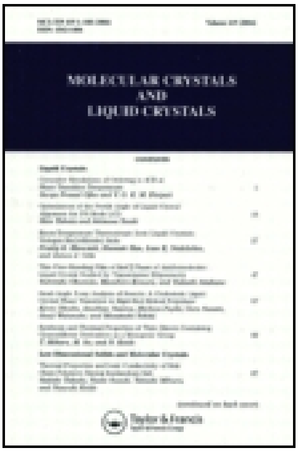

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Ellipsometric Measurements of the Optical Properties and Dynamics of Electrochemical Conversion in Films of Polyaniline

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Ellipsometric Measurements of the Optical Properties and Dynamics of Electrochemical Conversion in Films of Polyaniline

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We report ellipsometric measurements on films of polyaniline grown galvanostatically on platinum electrodes in HCl solutions. The films were characterized optically *in situ* and under potential control. They were also studied while undergoing electrochemical conversion between the bleached (insulating) and colored (conducting) forms induced by an applied bias. We show that ellipsometry is capable of providing unique information on the details of the electrochemical film conversion process. We also show that these films present strong similarities in both ellipsometric and voltammetric behavior with hydrous oxide films undergoing similar voltage-driven color-bleach cycles.

I. INTRODUCTION

Recent interest in conducting polymeric films on metal electrodes has originated from their possible applications in batteries,[1] as protective conducting electrode coatings,[2] as well as active materials in display devices[3] or in chemical sensor applications.[4] For the last two of these potential applications electrochemical switching of light absorption or of the electronic conductivity, respectively, is the basic physicochemical phenomenon examined. Both of these cases can be effectively studied by monitoring the optical properties of the films as a function of the many variables controlling their behavior.

Ellipsometry is one of the techniques that has been applied to the study of polymeric layers on electrode surfaces.[5] Compared with the more commonly used transmission spectroscopic techniques, ellipsometric analysis yields information on both the real and imaginary parts of the complex index of refraction, as well as on the thickness of the electropolymerized film.[6] Also, since ellipsometry is employed in a reflection mode, this technique can be used for the study of films formed on ordinary bulk metal electrodes. Furthermore, details of the process of electrochemical conversion in the film can be studied with this method.[7]

We present in this contribution results of an ellipsometric investigation of polyaniline (PANI) films, formed galvanostatically on Pt electrodes in HCl solutions.[3] We show that there are some strong similarities in both the voltammetric and the ellipsometric behavior of polymeric films and hydrous oxide films undergoing similar voltage-driven color-bleach cycles. Such similarities help to draw further conclusions on the details of the mechanism of electrochemical film conversion.

II. EXPERIMENTAL

Ellipsometry is an optical technique that measures variations in both the amplitude and phase parameters of a specularly reflected light beam.[6,8] It allows optical probing of films grown electrochemically on bulk metal electrodes, *in situ*, and while under an applied potential. The optical properties of the film are revealed by comparing the ellipsometric parameters of the reflecting metal substrate with and without film, as shown schematically in Figure 1. Both the real and imaginary components of the complex index of refraction (or complex dielectric constant) of the film are evaluated from ellipsometry, as

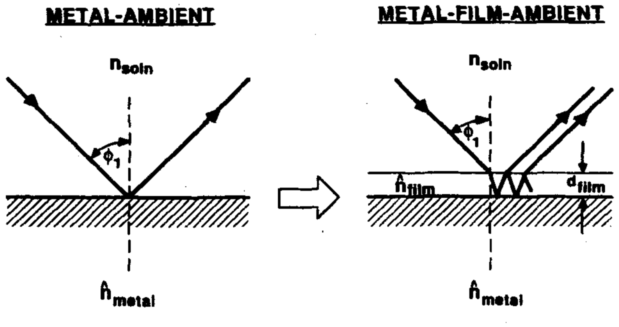

FIGURE 1 Schematic representation of the ellipsometry experiment. Prior to film growth, polarized light is reflected from the solution/substrate interface. Changes in the state of polarization of the reflected beam as a result of film growth are measured next. The optical parameters and thickness of the film are obtained from the ellipsometric parameters measured for the filmed and bare substrate.

well as the film thickness. The procedure that we have employed in this evaluation is described in the Appendix.

The automatic computer-controlled ellipsometer employed in this work is shown schematically in Figure 2 and has been described in detail elsewhere.[9] The present version is based on a photoelastic modulator operating at 50 kHz, and allows measurements in the near UV-visible-near-IR with 10 ms resolution. This was sufficient to avoid any instrumentation-related lag in potential cyclic experiments run at e.g. 50 mV/s. The wavelength domain used in the experiments reported here was 350–650 nm. The Pt electrode employed was a vertical disk, mounted on a Pt wire, spot-welded to the rear face of the disk. The disk was polished to good mirror finish with diamond paste using ethylene glycol as a lubricant. This was followed by thorough cleaning in methanol, chromic acid and distilled water. The aniline was purified by distillation in inert atmosphere at a reduced pressure.

The reference ellipsometric readings for the 'bare' Pt surface prior to polymeric film growth were taken in the 2 M HCl + 1 M aniline aqueous solution under a cathodic applied potential of − 0.1 V vs. the silver wire reference electrode. PANI film growth was performed galvanostatically from the same solution at 77 μA/cm^2 (of geometric area of the Pt electrode). Following each stage of galvanostatic growth—

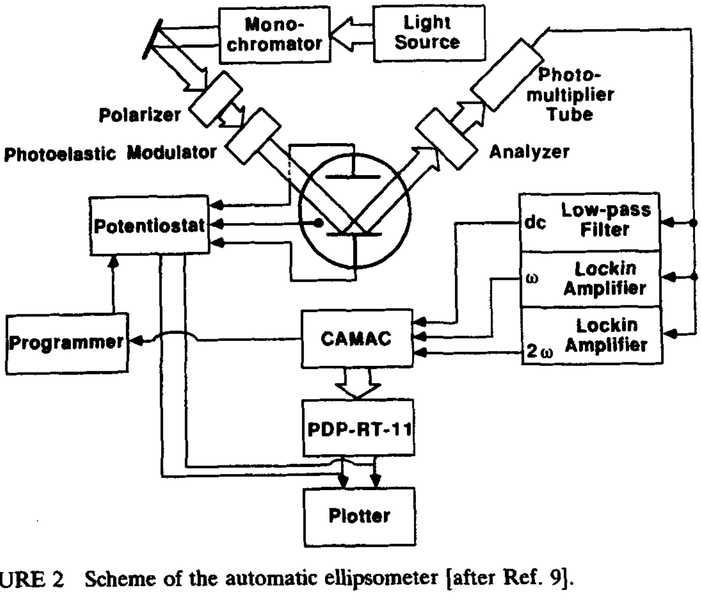

FIGURE 2 Scheme of the automatic ellipsometer [after Ref. 9].

typically 90 seconds—the current was interrupted and ellipsometric readings were taken under a pair of cathodic and anodic biases—usually 0 V and 0.52 V—corresponding to the bleached and colored forms of the PANI film. Ellipsometric readings had to be taken at potentials below 0.55 V (vs. the silver wire reference electrode) so that no further anodic growth would result during the optical measurements (as could be verified from the constant ellipsometric readings). Also, to avoid further growth and/or film modification, it was found that even for the limits mentioned, the potential had to be scanned, e.g. at 50 mV/s, rather than pulsed between the constant cathodic and anodic applied potentials. When the Pt surface was clean and the aniline freshly distilled, satisfactory fits of the ellipsometric results to a model that assumes thickness-independent optical properties were obtained in the thickness range 10–200 nm.

Ellipsometric conversion curves at a given film thickness were obtained by recording the continuous variation of the ellipsometric parameters Δ and Ψ as a function of potential during a triangular scan at 50 mV/s between 0 and 0.52 V. Since the optical effects recorded are rather large, only five repetitions, or less, of such scans were sufficient to achieve excellent signal-to-noise ratios. From the variations of Δ and Ψ vs. voltage a plot of Ψ vs. Δ, corresponding to the scan between 0 and 0.52 V (for a particular film thickness), could be generated by the computer.

After completion of an electrochemical-ellipsometric growth and conversion experiment the PANI film could be removed by immersion of the coated Pt electrode in hot chromic acid. Complete removal was tested before a subsequent experiment by recording the Pt disk voltammogram in 0.5 M H_2SO_4.

III. RESULTS

A. Optical properties of PANI films

A uniform film growth model was usually used for the analysis of the ellipsometric results (see the Appendix). The basic assumption in this model is that the optical properties of the PANI film under a constant applied bias do not vary with film thickness. Under this assumption the complex refractive index and thickness of both the colored and bleached forms of the PANI film could be evaluated based exclusively on the ellipsometric results. Figures 3–5 show results of fits of the ellipsometric readings at eight stages of galvanostatic film growth,

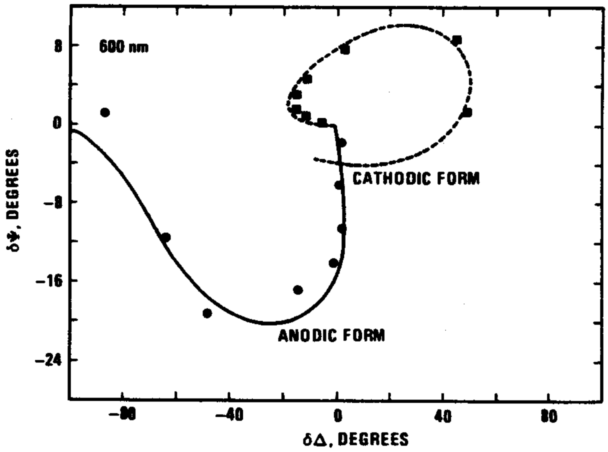

FIGURE 3 Computer fit of the experimental ellipsometric readings recorded during galvanostatic growth of PANI films using a uniform film-growth model at a wavelength of 600 nm; at 0 V, n_f = 1.56, k_f = 0.03; at 0.52 V, n_f = 1.17, k_f = 0.20.

assuming uniform growth. The assumption of thickness-independent optical properties is supported by the quality of the fits. The real part, n_f, of the complex index of refraction of the film found for the transparent form (at 0 V) is around 1.6 (1.56 at a wavelength of 600 nm), and the imaginary part, k_f, is close to zero (0.03 at 600 nm). Because of the optical transition typical of the anodic form of PANI,[3] switching the potential to 0.52 V results in a marked increase of k_f (to 0.20 at 600 nm). In addition, the increase of k_f is always accom-

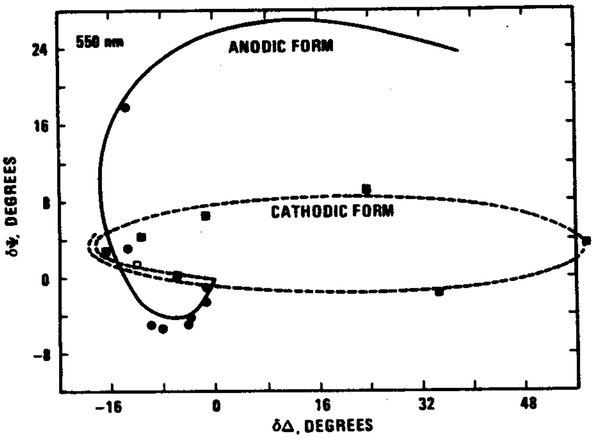

FIGURE 4 Same as Figure 3 at 550 nm; at 0 V, n_f = 1.62, k_f = 0.01; at 0.52 V, n_f = 1.34, k_f = 0.09.

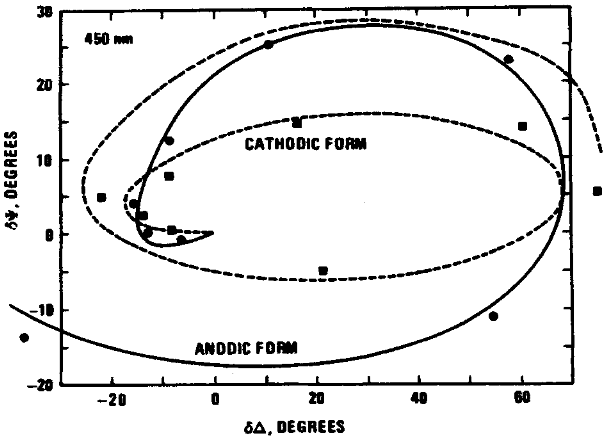

FIGURE 5 Same as Figure 3 at 450 nm; at 0 V, $n_f = 1.65$, $k_f = 0.05$; at 0.52 V, $n_f = 1.43$, $k_f = 0.12$.

panied by a decrease of n_f (to 1.17 at 600 nm). Film thicknesses in this experiment, as evaluated from the analysis of the same ellipsometric measurements, varied between 15 nm (stage 1) and 150 nm (stage 8).

Some variations in the optical properties of galvanostatically grown PANI films were found in repeated growth experiments. The value of n_f obtained for the bleached form of the film was typically 1.6 or somewhat higher, but values[7] as low as 1.48 were obtained in some of the growth experiments. The corresponding values of k_f, for the anodic film, were also somewhat lower. However, in most of the growth experiments the fit to the uniform growth model was of a quality similar to that shown in Figures 3–5 (for an example of non-uniform growth see Section IV C). The main features of an increase in k_f and a substantial accompanying decrease in n_f due to the anodic conversion were always reproduced.

B. Ellipsometric results recorded in potential scanning experiments

Figure 6 shows the variations of the current (solid curve), the charge (dotted line) and the ellipsometric parameters Δ (dashed) and Ψ (dashed-dotted) recorded during a triangular scan of the potential for a Pt electrode coated with a PANI film. For the wavelength region between 350 and 650 nm and for film thicknesses up to 200 nm the dependence of Ψ on V has always been found to be of the simple form depicted in Figure 6. The continuous lowering of Ψ with anodic potential reflects the increased light absorption in the film with in-

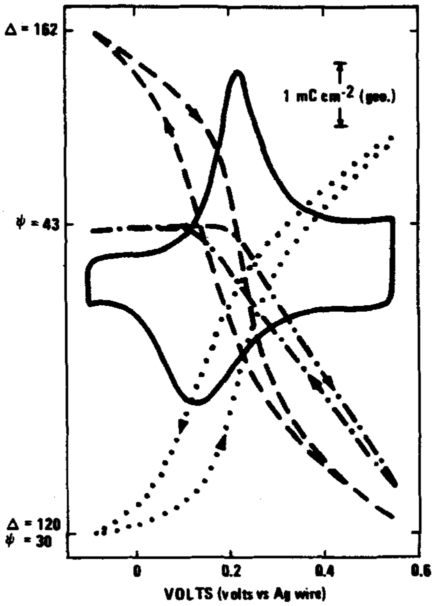

FIGURE 6 Variation of current (solid), charge (dotted), $\delta\Delta$ (dashed) and $\delta\Psi$ (dashed-dotted) during a triangular cycle at 50 mV/s for a Pt electrode covered by a film of polyaniline *ca.* 80 nm thick, immersed in aqueous 2 M HCl solution. Optical measurements taken at λ = 550 nm and ϕ_1 = 60 deg.

creasing injected anodic charge. The decrease of Δ with anodic potential shown in Figure 6 reflects the lowering of n_f during anodic film conversion.

Rather than plot the changes of Δ and Ψ vs. V in a manner that mimics voltammetry, as done in Figure 6, the variations of the two ellipsometric parameters during the voltage-driven film conversion can be plotted against each other. Such 'ellipsometric conversion curves' have been used by Hopper and Ord,[10] and by Clayton and DeSmet[11] to analyze conversion processes in oxide films. We have briefly described such plots before in a short communication.[7] Figures 7 and 8 show simulated and experimental ellipsometric conversion curves for PANI films of two different thicknesses. In the simulations three possible modes of anodic film coloration were considered, as described schematically in Figure 9: (A) coloration develops from the film/substrate interface towards the film/solution interface; (B) coloration develops from the film/solution interface towards the film/substrate interface; and (C) coloration develops uniformly throughout the volume of the film. The simulation for modes (A) and (B) is

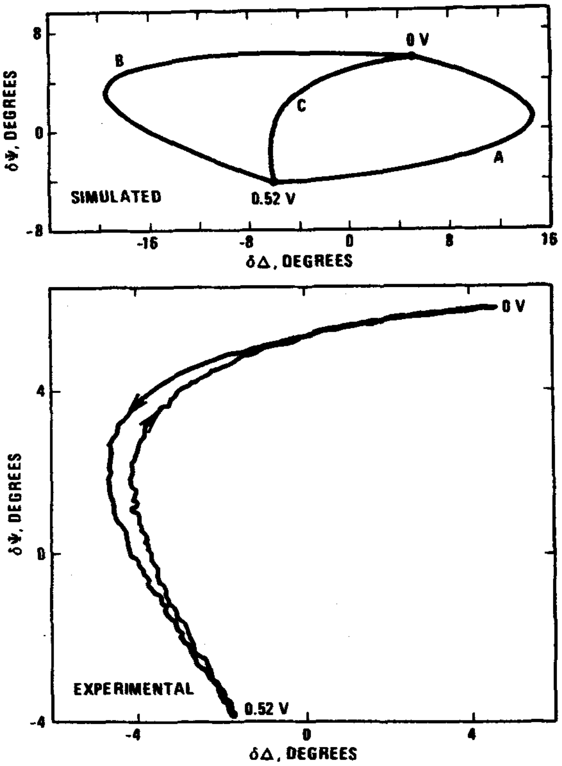

FIGURE 7 Simulated and experimental ellipsometric curves for the electrochemical conversion of a PANI film on Pt in 2 M HCl. Optical properties of the film at 0 V: $n_f = 1.48$, $k_f = 0.013$; at 0.52 V: $n_f = 1.30$, $k_f = 0.060$. Film thickness: 115 nm. Simulated curves A, B and C correspond to the respective conversion modes shown in Fig. 9.

based on a dual film system, using 100 gradual steps in which the thickness of the colored part increases at the expense of the bleached part of the film, keeping the overall thickness constant. The simulation of mode (C) is based on a gradual (100 step) shift between the complex refractive indices of the bleached and colored forms of the film, taking place uniformly throughout a film of constant thickness. The expressions used for the simulations of the three modes of coloration, based on a single (mode C) or a dual film structure (modes A and B) are standard.[8] The optical properties of the 'fully colored' and 'fully bleached' parts of the film used in the simulations were always those evaluated for the same PANI layer from the static ellipsometric measurements taken at several growth stages at 0 and 0.52 V.

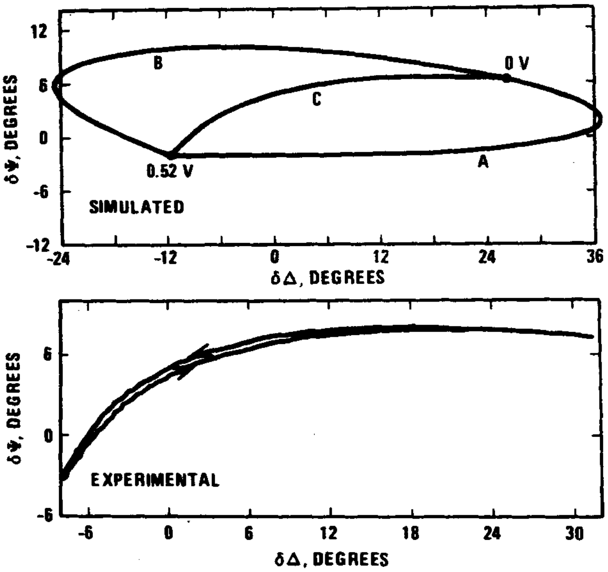

FIGURE 8 Same as Figure 7, for a film thickness of 150 nm.

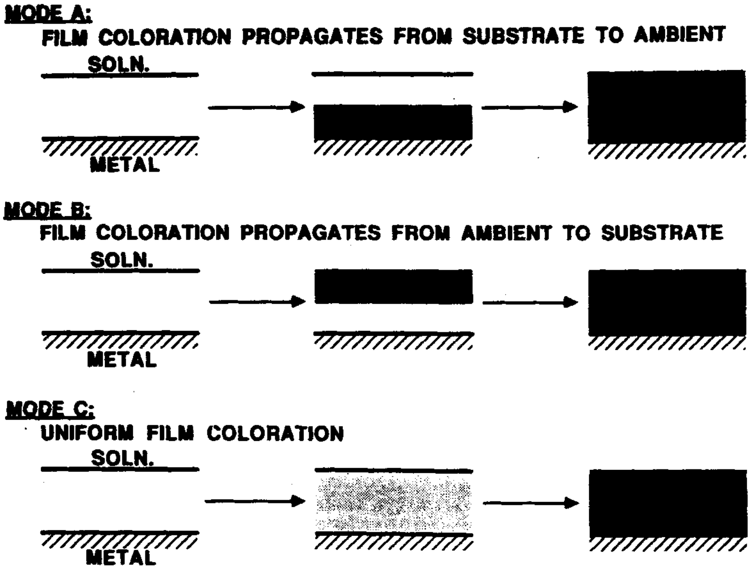

FIGURE 9 The three possible modes of electrochemical film conversion that can be differentiated by ellipsometric measurements. Mode A corresponds to a process of charge injection limited by electron transport, Mode B to a rate limited by insertion of ions from solution, and Mode C to a case of high levels of both ionic and electronic transport rates within the film.

Since the conversion process requires both electronic and ionic transport to or from sites within the film, the conversion mode would depend on the relative levels of the electronic and ionic conductivities. PANI films have been reported to be poor electronic conductors in the cathodic form.[4] This seems to imply mode (A) of anodic coloration. Instead, as Figures 7 and 8 indicate, the experimental ellipsometric curves (for the wavelength region covered and for film thicknesses up to 200 nm) conform well with mode (c) of film conversion (i.e., with the coloration spreading *uniformly* throughout the film). The experimental curves actually bear no similarity to the simulations based on the propagation of coloration from one interface to the other.

IV. DISCUSSION

A. Optical properties

The index of refraction of the bleached form of the polymeric film can be considered as a criterion for the density (i.e., the compactness) of the layer. Arwin *et al.*[12] have quoted $n_f = 1.65$ as a relatively high value of n_f for a polymer of a similar nature. As specified above, similar values were frequently found for PANI under 0 V bias, but lower values were found in some of the growth experiments. This implies different degrees of compactness and different solvent content in repeated experiments. It appears that very early stages of growth determine the film morphology. With few exceptions, once a film of a given value of n_f started to grow it continued to maintain a similar density, so that the ellipsometric growth curve (Figures 3–5) conformed reasonably well with the uniform growth approximation up to thicknesses of 200 nm.

The values of k_f found for the PANI films is very similar in magnitude to those evaluated for the colored forms of electrochromic hydrous oxide films, such as anodic Ir[13] or anodic Ni[10] oxides. These values of $k_f \approx 0.1$ at 600 nm correspond to an absorption coefficient of $\alpha = 2 \times 10^4$ cm^{-1}. The voltammetric charge density, expressed in Cb cm^{-3}, in PANI films grown in aqueous HCl (Figure 6), is analogous to that found for hydrous anodic oxide films with similar values of α.

A very reproducible effect detected in this work is the lowering of n_f which accompanies the increase of k_f during coloration. In fact, n_f for the anodic form of PANI could become lower than n_{H_2O} at wavelengths between 550 and 650 nm. The longer the wavelength the stronger is the lowering of n_f during coloration. While not considered in previous treatments of similar film conversion processes, this behavior is fully expected from the basic physics of the introduction of a new optical oscillator into a material. The expected shape of k_f vs. photon energy for a single optical oscillator is close to a Lorentzian, while the dispersion of n_f is expected to show an increase as the peak of k_f is approached form the low photon energy side and a decrease as it is approached form the high photon energy side.[14] For the wavelength region employed in this work, n_f was found to decrease with the anodic introduction of absorption, the effect being stronger at lower wavelengths. This is the expected behavior if the peak of k_f is located at a lower photon energy. In fact, the peak of k_f for PANI films lies at around 740 nm, as reported from transmission spectra.[3]

Finally, the similarity of the optical properties and of the transmission spectra of the polyaniline and of the hydrous oxide films, such as anodic Ir oxide, possibly originates from a similar morphology of both kinds of films. It can be described as a denser phase, which in the case of thicker polyaniline films has been reported to be in the form of fibers[5] forming a network within the film, surrounded by a less dense phase which may be quite close in properties to the electrolyte solution in which the film is immersed. The optical and electrical properties of such a composite film can be described in terms of effective-medium theory,[15] as done before for hydrous Ir oxide.[16] Within this theory one may determine the optical properties (as well as the electronic conductivity). In the treatment of Kang and Shay[16] the properties of metallic IrO_2, assumed to form the denser network within the porous hydrous film, were used in the calculation of the optical properties of the colored hydrous Ir oxide film. Such a calculation[16] predicts a resonance around 700 nm. In it, the critical parameters are the plasma frequency of the electrons in the metal (IrO_2 single crystal), the volume fraction of the metal in the composite film, and the dielectric constant of the solution in the pores. In the absence of the knowledge of the plasma frequency for ideally dense (metallic?) polyaniline, one can only argue that the similarity of the transmission spectra of the colored forms of PANI and of the hydrous oxide, (both exhibit a major peak *ca.* 700 nm[3,16]), plus the nearly equal values of k_f, suggest that the optical behavior of polyaniline films grown in aqueous solutions may be due to a similar composite film in which metallic regions are surrounded by regions close in composition to the electrolyte solution.

B. The film conversion process

Some points regarding this specific subject have been briefly discussed above. Figures 7 and 8 show that the simulated ellipsometric conversion curves have distinctly different forms for the three modes of film conversion. The experimental curves conform well with a uniform increase of coloration throughout the volume of the film, and do not resemble at all the other two possible modes. Deviations from an ideal fit of the simulated to the experimental curves for mode (C) of film conversion could be due to slight variations in film thickness during the conversion process, and/or to some uncertainty in the optical properties of both the bleached and the colored forms of the film, as derived from the uniform growth approximation. Since any of these reasons could cause such small deviations no attempt was made to refine the simulation. It should be stressed that the quality of the fit does rule out thickness differences between the bleached and colored forms larger than 10–15%.

Similar results of uniform coloration have been obtained before for anodic hydrous Ni, as well as Ir, oxide films[10,17] which undergo similar color-bleach cycles. Both of these films are known to have composite internal porous (or spongy) structures, which allow fast ionic transport. The electronic conductivity may vary as a function of bias and is expected to be much lower for the bleached form of the oxide. Microscopic examination of thicker PANI films revealed a network of denser fibers within the film.[5] Measurements of the electronic conductivity revealed low conductivity for the bleached (cathodic) form of PANI. An interesting question which arises from the reported low electronic conductivity of bleached PANI is why mode (A) of film conversion is not preferred in the anodic conversion process. If electron transfer through the film is a very slow process, the region closest to the metal substrate is expected to be the first to be active in the electron ejection process, with the coloration spreading gradually towards the film/solution interface. However, the ellipsometric results shown here for the conversion process in PANI films, as well as those reported for hydrous anodic Ir or Ni oxides,[10,17] demonstrate that the coloration process is rather *uniform* along the direction perpendicular to the surface. The explanation lies apparently in the following details of the anodic conversion process. It seems that the anodic process begins in the PANI film by the injection of a relatively small anodic charge, which is sufficient to increase the electronic conductivity significantly. Following this initial charge injection, the rest of the combined electronic/ionic process can proceed uniformly throughout the volume of the film, since both the electronic

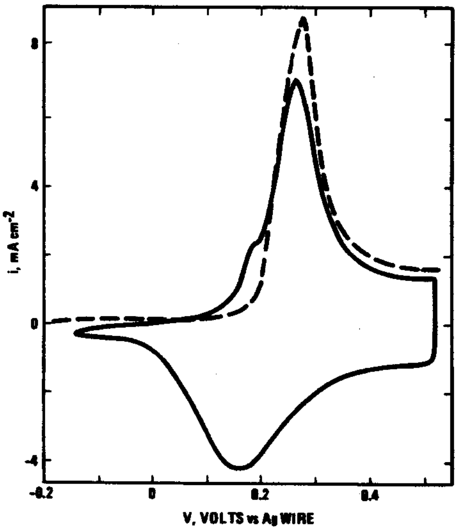

FIGURE 10 Voltammograms recorded for PANI film *ca.* 250 nm thick on Pt in 2 M HCl. Solid curve: multiscans at 50 mV/s, showing the anodic irreversible prepeak. Dotted curve: anodic scan following holding for 2 min at −0.2 V, showing the resulting increase in overpotential required for anodic conversion.

and the ionic resistances between charging sites anywhere within the film and the ohmic contact or the bulk electrolyte become very small.

Examination of the PANI voltammogram (Figure 10) supports the above suggestion on the sequence of steps in the anodic coloration process. An irreversible anodic prepeak starts to be well resolved for PANI films thicker than 100 nm. Following this prepeak or shoulder, the rest of the anodic charge passes readily in the form of a relatively sharp peak. This anodic prepeak seems to result from the initial increase of conductivity through the film, as discussed above.[18] The overpotential required to inject the initial anodic charge through a phase of low electronic conductivity contributes to the apparent asymmetry of the voltammogram. The reverse process, cathodic bleaching, starts from a film of high electronic conductivity, thus the reduction peak is simple in form and could arise from a simple distribution of electrochemical potentials of charging sites within the film, with no further complication due to transport limitations. Nevertheless, as full reduction is approached, the cathodic process does become slow and can be brought closer to completion by longer cathodic holding, e.g. at −0.2 V. As shown in Figure 10, cathodic holding results in a subsequent larger anodic overpotential required to 'trigger' the anodic conversion in the PANI film. This is due to the lower electronic conductivity reached by such holding.

These voltammetric features bear a striking similarity to those reported for Ir and Rh anodic hydrous oxide films.[13] In fact, an identical anodic irreversible prepeak appears in the voltammograms of these anodic oxide films.[13] This prepeak is the main reason for the asymmetry in the voltammograms recorded during the oxide film conversion process. Interestingly, such a prepeak appears only if the cathodic form of the oxide is indeed fully bleached. For some structures of Ir oxide which do not allow complete cathodic bleaching, the prepeak does not appear and the voltammogram becomes symmetric.[16]

This strong similarity in voltammetric behavior further substantiates the suggestion that the origin of the hysteresis in the conversion process on the potential scale is not 'chemical' in nature, but has to do with the low electronic conductivities of the bleached forms of all these different films.[18]

A final point to be discussed addresses the possibility of resolving a special feature in the ellipsometric conversion curve which parallels the irreversible anodic prepeak in the voltammogram. The conversion scheme that we have proposed implies that the early anodic step in the coloration process should propagate in the bleached film from substrate to electrolyte (mode A). Evidence of such an early optical effect would be in the form of a deviation from the ellipsometric curve expected for uniform coloration. Unfortunately, this initial coloration effect is very small and overlaps with the very much larger optical effect which proceeds through the film uniformly, making it is difficult to resolve. In some cases, a special feature in the ellipsometric conversion curve did appear to be associated with the early stage of anodic coloration, but it could not be repeated reproducibly.

C. More complicated growth patterns

In a few experiments, the anodic growth of the PANI film was much less uniform than reported above. This manifested itself in lack of convergence when attempting to solve the ellipsometric equations assuming properties independent of thickness. Nevertheless, one can still solve (see the Appendix for details) for each individual stage of film growth provided measurements of the relative change in reflected intensity are added to the regular ellipsometric measurements. This can be done on the experimental setup described schematically in Figure 2.

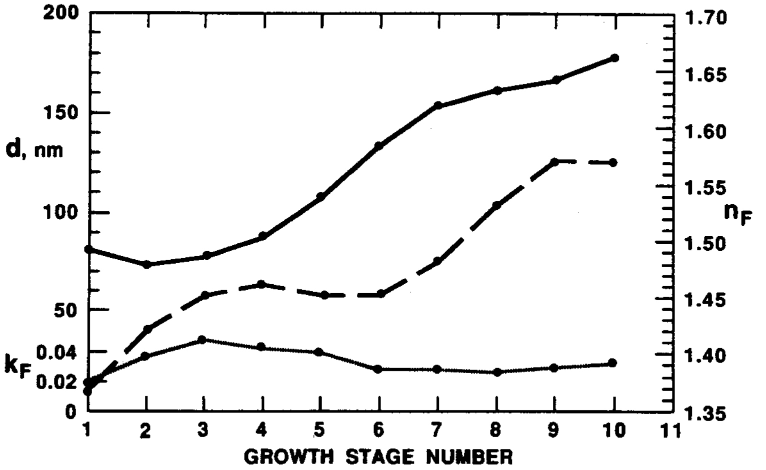

FIGURE 11 Variations in film thickness (solid), n_f (dashed) and k_f (dotted) during the nonuniform growth of a PANI film, as evaluated from combined ellipsometric-reflectometric measurements.

For nonuniform growth, the optical measurements reveal details of the growth pattern. An example is presented in Figure 11, where we report variations of film thickness (solid line), the real part of the index of refraction (dashed curve), and the imaginary part of the refractive index (dotted line). The curves clearly show the nonuniformity of the growth process.[19] Growth seems to begin on a small part of the surface, resulting at first in a rather thick apparent film with an index of refraction close to that of the solution. This suggests a mixed solution/polymer film with a very substantial volume fraction of solution. This is followed by an increase of n_f at almost constant film thickness, much as one would expect for lateral overlap of growth centers. Between growth stages 3 and 7, growth takes place at almost constant n_f and beyond stage 7 the film again densifies, keeping the thickness almost constant.

Figure 12 shows experimental and calculated plots of $\delta\Psi$ (circles) and the reflected intensity ratio $(R_s + R_p)_{film}/(R_s + R_p)_{metal}$ (squares) vs. $\delta\Delta$. The solid lines correspond to the computer generated solutions for the uniform growth of a film with the final optical properties (stage 10). The dashed curves represent the solutions for uniform growth of a film with the initial optical properties. The figure demonstrates that this film tended to approach ordinary properties of PANI films towards the end of the growth process (*ca.* 180 nm), but strong deviations from such properties were found at earlier stages

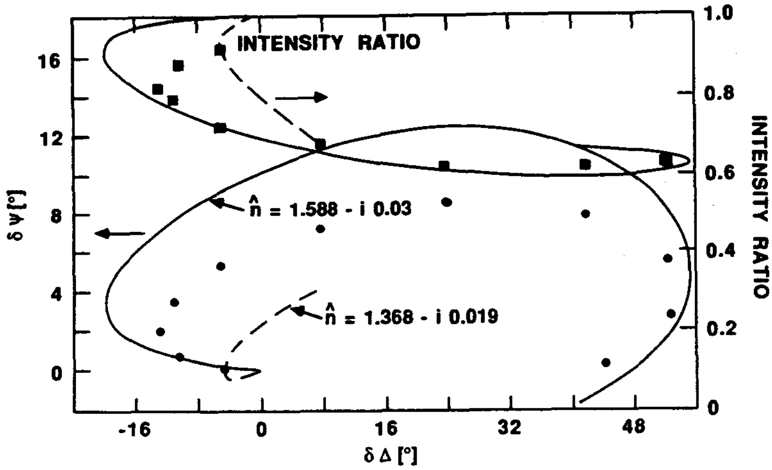

FIGURE 12 Experimental points and computer-generated curves for the same film as in Figure 11. Circles: experimental ($\delta\Delta,\delta\Psi$) points. Squares: experimental ($\delta\Delta$, Intensity ratio) points. Solid curves: calculated solutions for the uniform growth of a film with the final optical properties (growth stage 10). Dashed curves, calculated solutions for a film with the initial optical properties (stage 1).

of growth. A similar 'nucleation and densification' mode of electrochemical growth was described recently by Hamnett and Hillman[20] for films of polythiophene.

V. CONCLUSIONS

Ellipsometry is a powerful tool in the *in situ* analysis of the growth pattern, the optical properties and the film conversion processes in conducting polymer films. Our results show that PANI films usually grow uniformly, i.e., with optical properties that do not vary with thickness up to film thicknesses of 200 nm. In some cases, however, nonuniform film growth was observed. The propagation of coloration in films of PANI is uniform through the volume of the film due to high ionic and electronic conductivities during most of the conversion process. The similarity between the optical properties of PANI films in the visible region and their film conversion characteristics and those of some hydrous oxide films is quite striking. It demonstrates that the composite nature of the films and the insulator-conductor transition are two strong characteristics that can generate similarities in the electrochemical and optical behavior of films of very different chemical origins.

Acknowledgments

This work has been carried out under the auspices of the United States Department of Energy. E.A.T. gratefully acknowledges the support of the Brazilian CNPq.

Appendix

The calculation of the complex index of refraction and thicknesses of the films was performed using a nonlinear least-squares (Levenverg-Marquardt) algorithm,[21] with standard ellipsometric formulas for a film/substrate system.[8] The optical problem can be solved within the uniform growth model without additional (non-optical) assumptions on the nature of the film.[22] If the ellipsometric readings are examined at N different stages of growth, the overall number of unknown parameters is $N + 2$. These unknowns correspond to n_f, k_f (assumed to be independent of thickness) and the film thicknesses, d_i. On the other hand, there are $2N$ experimental readings obtained at the wavelength and angle of incidence employed. These consist of the N pairs, $(\delta\Delta_i^{exp}, \delta\Psi_i^{exp})$, of ellipsometric angles ($\delta\Delta$ is the difference between the actual value of Δ for the i-th stage and that of the bare substrate). The fit is performed by minimizing the quantity

$$\chi^2 = \sum_{i=1}^{N} ([1 - \delta\Delta_i/\delta\Delta_i^{exp}]^2 + [1 - \delta\Psi_i/\delta\Psi_i^{exp}]^2),$$

where $\delta\Delta_i$ is the calculated value at the i-th growth stage. The fits shown in Figures 3–5 were obtained using this procedure.

In the case of nonuniform growth one would like to calculate the individual values of n_f, k_f and d for each growth stage. This can be accomplished if in addition to the two ellipsometric angles one also measures the reflectivity (intensity) ratio $\xi = (R_s + R_p)_{film}/(R_s + R_p)_{metal}$. In this case, for each stage one has three unknowns which can be solved for using, for example, the Newton-Raphson method. Indeed, this method has been used previously in very thin films.[23] In the case of polyaniline, however, we have found that the quantity ξ is quite insensitive to variations in the thickness and the complex index of refraction for the cathodic form of the film. This leads to extremely small derivatives which render the Newton-Raphson method useless for all practical purposes.

For this reason we opted to fit the individual growth stages by means of nonlinear least-squares analysis. This, however, does not eliminate the problems associated with the small derivatives of ξ.

Indeed, nonlinear least-squares fits using $\delta\Psi$, $\delta\Delta$ and ξ for transparent (or slightly absorbing) films suffer from poor convergence and are unstable. Fortunately, a solution to this problem can be found with the information already available. In particular, instead of using the ratio ξ we can use the reflectivities for pure *p*- and *s*-polarized light. These, together with $\delta\Psi$, $\delta\Delta$, lead to well behaved fitting procedures with excellent sensitivity to the optical properties of the films. In this case, one can easily show that the reflectivities for the *i*-th growth stage are given by $R_s = \xi(R_s + R_p)_{metal}/(1 + \tan^2\Psi_i)$ and $R_p = R_s\tan^2\Psi_i$. Thus, the problem can be solved by minimizing the quantity

$$\chi^2 = [1 - \delta\Delta/\delta\Delta^{exp}]^2 + [1 - \delta\Psi/\delta\Psi^{exp}]^2 + [1 - R_s/R_s^{exp}]^2 + [1 - R_p/R_p^{exp}]^2.$$

This equation was employed in the calculation of the fits shown in Figures 11 and 12.

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