ResearchGate

See discussions, stats, and author profiles for this publication at: https://www.researchgate.net/publication/239717562

A Study of Gold-Coated Glass as Electrodes for Electropolymerization of 3Methylthiophene

ARTICLE *in* LANGMUIR · AUGUST 2001

Impact Factor: 4.46 · DOI: 10.1021/la0101090

CITATIONS
9

READS
6

2 AUTHORS:

Débora Gonçalves
University of São Paulo
61 PUBLICATIONS **678** CITATIONS

SEE PROFILE

E. A. Irene
University of North Carolina at Chapel Hill
255 PUBLICATIONS **5,429** CITATIONS

SEE PROFILE

Available from: Débora Gonçalves
Retrieved on: 31 January 2016

A Study of Gold-Coated Glass as Electrodes for Electropolymerization of 3-Methylthiophene

Débora Gonçalves* and Eugene A. Irene

University of North Carolina at Chapel Hill, Department of Chemistry, CB#3290, Chapel Hill, North Carolina 27599-3290

Received January 22, 2001. In Final Form: May 9, 2001

The viability of using Au surfaces made from Au evaporated on glass plates with a Cr underlayer was studied for the electropolymerization of 3-methylthiophene. Poly-3-methylthiophene films were prepared using cyclic voltammetry in an acetonitrile medium by varying the potential range, monomer concentration, etching treatment of Au, and the electrolyte salt. After a relatively high potential was applied, which is necessary to oxidize the monomer, dissolution of the Au overlayer occurred, particularly when tetrabutylammonium tetrafluoroborate was used as the electrolyte salt. Strong evidence points to contaminants such as chloride as the Au dissolution initiator. The pretreatment of the electrode surface also affected the voltammetric response of Au, because dissolution is accelerated after using wet chemical etches. X-ray photoelectron spectrometry was used to verify the exposure of the Cr underlayer by dissolution of Au.

Introduction

Particularly after Tourillon and Garnier in 1982,[1] the electrochemistry of polythiophene films has been extensively investigated in order to elucidate the growth steps under different synthesis conditions and the electroactive response in monomer-free solutions. In most of the recent papers, polythiophene and derivatives have been prepared by potentiostatic or galvanostatic deposition on platinum or ITO (indium-doped tin oxide) electrodes.[2] As compared with the parent polythiophene, poly-3-methylthiophene (PMT) displays high electrical conductivity along with environmental stability.[3,4] In addition, its wide use is justified by a straightforward method of electrosynthesis owing to a lower oxidation potential as compared to that required of its parent thiophene. Most applications of PMT films, that involve photovoltaic cells[5] and organic two-layer diodes,[6,7] are based on the films being electrochemically deposited onto evaporated Au electrodes. The crucial issue arising from the use of Au-coated substrates is the possibility of metal dissolution/corrosion under the application of the high potentials that are necessary to oxidize these types of monomers. In fact, as will be shown herein, the Au overlayer dissolves in certain media during the electropolymerization of 3-methylthiophene. However, studies of Au dissolution are sparse. Recently, Skompska[8] verified dissolution of bulk Au electrodes in a medium of propylene carbonate containing 3-dodecylthiophene and lithium perchlorate. Furthermore, previous studies on the adsorption of thiols on evaporated Au substrates[9−13] enumerate reasons to study the Au surface before chemical adsorption processes take place. The Au electrode may dissolve not only during the polymer film formation but also during manipulation of the as-prepared devices, particularly because most of the polymers used, for example, for field-effect transistors, are partially doped. Therefore, the role of traces of impurities not intentionally added to the electrolyte solution such as Cl^- and SO_4^{2-} on Au dissolution is an important matter. Another issue is the exposure of underlying adhesion layers such as Ti, W, and Cr that may initiate severe interface problems.[14,15] The present study was directed to verify that the dissolution of Au occurs in an acetonitrile medium containing tetrabutylammonium tetrafluoroborate rather than lithium perchlorate, owing to the unexpected presence of traces of impurities in the tetrafluoroborate. Our main concern was to verify whether the early stages of film growth were affected by Au dissolution, inasmuch as the potential necessary to oxidize 3-methylthiophene is high enough to initiate electrode surface modifications. Specific experiments were performed to elucidate how the exposure of the Cr underlayer affects the voltammetric response of Au-coated electrodes.

Experimental Section

Electrochemistry and Materials. 3-Methylthiophene was electrochemically polymerized on Au electrodes that were evaporated onto glass plates (usually 1.0 cm^2) using a standard three-electrode, one-compartment electrochemical cell. The electrolyte solution was a nonaqueous acetonitrile medium containing 0.1 mol L^{-1} tetrabutylammonium tetrafluoroborate

* Corresponding author. Permanent address: Instituto de Física de São Carlos, Universidade de São Paulo, CP 369, 13560-970, São Carlos - SP, Brazil. E-mail: gdebora@if.sc.usp.br.

(1) Tourillon, G.; Garnier, F. *J. Electroanal. Chem.* **1982**, *135*, 173.
(2) Berlin, A. In *Electrical and optical polymer systems − fundamentals, methods, and applications*; Wise, D. L., Wnek, G. E., Trantolo, D. J., Cooper, T. M., Gresser, J. D., Eds.; Marcel Dekker: New York, 1993; p 47.
(3) Sato, M.; Tanaka, S.; Kaeriyama, K. *J. Chem. Soc., Chem. Commun.* **1985**, 713.
(4) Hotta, S.; Soga, M.; Sonoda, N. *Synth. Met.* **1988**, *26*, 267.
(5) Uehara, K.; Ichikawa, T.; Serikawa, T.; Yoshikawa, S.; Ehara, S.; Tsunooka, M. *Thin Solid Films* **1998**, *322*, 198.
(6) Uehara, K.; Ichikawa, T.; Matsumoto, K.; Sugimoto, A.; Tsunooka, M.; Inoue, H. *J. Electroanal. Chem.* **1997**, *438*, 85.
(7) Uehara, K.; Ichikawa, T.; Maekawa, A.; Serikawa, T.; Nishiyama, N.; Tsunooka, M. *Thin Solid Films* **1995**, *263*, 263.
(8) Skompska, M. *Electrochim. Acta* **2000**, *45*, 3841.
(9) Ron, H.; Matlis, S.; Rubinstein, I. *Langmuir* **1998**, *14*, 1116.
(10) Ron, H.; Rubinstein, I. *Langmuir*, **1994**, *10*, 4566.
(11) Chechick, V.; Crooks, R. M.; Stirling, C. J. M. *Adv. Mater.* **2000**, *12*, 1161.
(12) Baker, L. A.; Zamborini, F. P.; Sun, L.; Crooks, R. M. *Anal. Chem.* **1999**, *71*, 4403.
(13) Creager, S. E.; Hockett, L. A.; Rowe, G. K. *Langmuir* **1992**, *8*, 854.
(14) Josowicz, M.; Janata J.; Levy, M. *J. Electrochem. Soc.* **1988**, *135*, 112.
(15) Ashwell, G. W.; Heckingbottom, R. *J. Electrochem. Soc.* **1981**, *128*, 649.

10.1021/la0101090 CCC: $20.00 © 2001 American Chemical Society
Published on Web 07/14/2001

($TBABF_4$) or lithium perchlorate ($LiClO_4$) (all purchased from Aldrich). The reference electrode was a Ag quasi-reference electrode (Ag-QRE) immersed in a glass tube containing the electrolyte salt in acetonitrile. The potential of Ag-QRE in 0.1 mol L^{-1} $LiClO_4$ was 54 ± 4 mV and in 0.1 mol L^{-1} $TBABF_4$ was 123 ± 2 mV versus SCE reference electrode. A platinum wire was used as counter electrode. The amount of water in acetonitrile was 0.002 vol % (20 ppm, labeled value) before adding molecular sieves (4 Å, Aldrich) treated at 300−400 °C for 48 h. The solvent was stored apart with other glass materials (cell and syringes) in a desiccator. The electrolyte salts were kept over P_2O_5. Before each electrochemical measurement, the solution was purged with nitrogen for at least 30 min. Accordingly, after each measurement the solutions were renewed and the cell was rinsed with acetonitrile, to avoid possible solution/cell contamination. All electrochemical measurements were performed using a Cypress OMNI 101 potentiostat with data acquisition software.

Gold Electrodes. The Au overlayers (usually 600 Å) were vacuum deposited on microscope glass plates that had evaporated Cr underlayers (usually 400 Å) at 1.4×10^{-6} Torr and deposition rates of 8 Å s^{-1} for Cr and 30 Å s^{-1} for Au. Although the thickness of the Cr overlayer can be considered larger than necessary for our purposes, thinner layers (e.g., 20−100 Å) sometimes led to diminished adhesion of Au on the glass plates. This problem will be discussed further. Prior to the metallization, the glass plates were cleaned with soapy water and then piranha solution (H_2SO_4/H_2O_2 30% 1:1) for 30 min with ultrasonic agitation. Unless described otherwise, the Au electrodes were cleaned by immersion in isopropyl alcohol in an ultrasonic bath for 30 min and dried with a stream of nitrogen. Other cleaning procedures included immersion of the electrodes in the following solutions: (i) dilute aqua regia ($HCl/HNO_3/H_2O$ 3:1:10) for 3, 5, or 7 min; (ii) SC (standard clean) ($NH_4OH/H_2O_2/H_2O$ 1:1:5) for 5 or 20 min; and (iii) piranha (H_2SO_4/H_2O_2 30% 1:1) for 5 min. These pretreatments were performed using an ultrasonic bath at room temperature just before each electrochemical experiment. The choice of these cleaning solutions was based on previously reported results about the adsorption processes of thiols on Au surfaces.[12,16]

Instrumentation. The X-ray photoelectron spectra (XPS) were acquired using a PHI 5400 series instrument equipped with a monochromatic Mg Kα X-ray source and coupled with a RBD model 147 data acquisition system. The chamber pressure was typically around 5×10^{-9} Torr. Spectroscopic ellipsometry (SE) measurements were carried out using a custom-built rotating analyzer spectroscopic ellipsometer from 250 to 850 nm at an incidence angle of 70°.

Results and Discussion

Final Potential. In Figure 1a are shown the voltammetric responses of Au-coated electrodes in an acetonitrile medium containing 3-methylthiophene and tetrabutylammonium tetrafluoroborate ($TBABF_4$) at two different potential ranges: 0.2−1.6 V versus Ag (curves I, up to three cycles) and 0.2−1.7 V (curve II, first cycle).

Between 0.2 and 1.6 V for curves I, the appearance of a well-defined peak at about 1.42 V (labeled A) is observed, which may correspond to the anodic dissolution of the bare Au electrode to Au(I) species. As the scan direction is reversed, a cathodic peak with a low current intensity appears only for the first cycle at 0.85 V (labeled C). For curve II (E_f = 1.7 V), the A peak is followed by an intense anodic current beyond 1.5 V due to the oxidation of 3-methylthiophene.

The two sets of data display the same feature for the A peak but with some differences, which are dependent on the surface state of the electrode. As the scanning continues in the reverse direction, one clearly notes a crossover current (loop), which is likely evidence for the nucleation of the polymer film on the electrode surface.[17] In this case, the electroactive area of the electrode increased rapidly upon monomer oxidation indicating that the value chosen of E_f is not sufficiently high to define an anodic peak but is high enough to promote the film growth. The absence of the peak C for curve II indicated reduction of a modified Au surface with a polymer film (instead of a bare surface) inasmuch as cation radicals formed from oxidation of 3-methylthiophene at higher potentials are unstable enough to undergo fast coupling reactions.

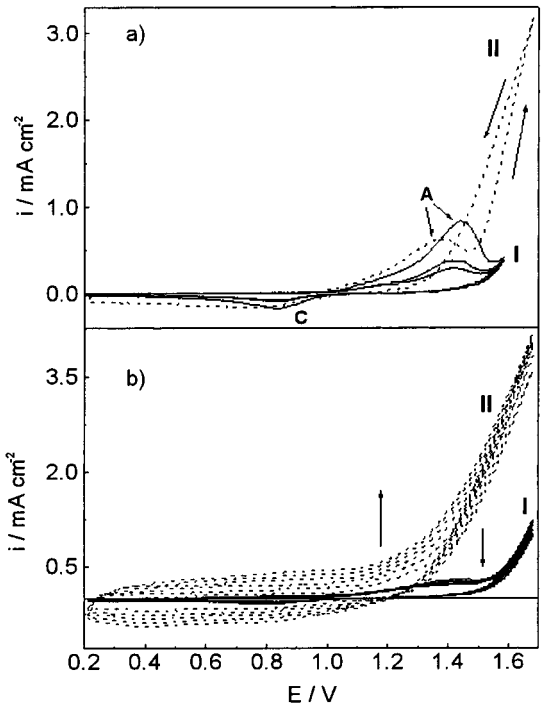

Figure 1. Cyclic voltammograms of Au-coated electrodes in acetonitrile medium containing 0.1 mol L^{-1} 3-methylthiophene and 0.1 mol L^{-1} $TBABF_4$ at different values of final potential (E_f): E_f = 1.6 V (curves I); E_f = 1.7 V (curves II); (a) first cycles; (b) successive cycles; v = 20 mV s^{-1}.

In Figure 1b are shown two sets of successive cyclic voltammograms for the same electrodes, both taken at E_f = 1.7 V. The value of E_f was raised from 1.6 to 1.7 V for curves I, because no visible film deposited on the electrode surface at E_f = 1.6 V. Even though the value of E_f was changed, the current density decreased with repetitive cycles (see arrows). In fact, a passive layer, formed after the first cycle at E_f = 1.6 V, prevented later stages of polymer growth.

We also tested other working electrodes, platinum rod and ITO (indium−tin oxide coated glass), in this same medium and a similar potential range (results not shown). In this case, the absence of the A peak on platinum reinforced our contention that this peak can be attributed to the oxidation of the bare Au electrode.

After the experiments at different potentials, two films with different appearances were obtained on Au: one, opaque and yellow (sample I), and the other, homogeneous and brown (sample II). The yellow film showed a narrow blue strip on the top film surface clearly evidencing exposure of the underlying Cr layer during the first cycles at a less positive value of E_f (1.6 V) (experiment I). As strong evidence of the Au removal in this case, the electrolyte solution became bluish after various cycles due to the exposure of the Cr underlayer. For experiment II,

(16) Liedberg, B.; Yang, Z.; Engquist, I.; Wirde, M.; Gelius, U.; Götz, G.; Bäuerle, P.; Rummel, R.-M.; Ziegler, Ch.; Göpel, W. *J. Phys. Chem.* **1997**, *101*, 5951.

(17) Downard, A. J.; Pletcher, D. *J. Electroanal. Chem.* **1986**, *206*, 147.

on the other hand, colored products appeared at the electrode/solution interface only during the first two cycles with the solution keeping its transparency after successive cycles. These colored products may indicate the presence of oligomers, which diffuse toward the electrode/solution interface and adsorb onto the electrode surface. Two complete cycles were enough to produce a visible colored polymer film.

Pioneering work[18] on nucleation of polythiophene on bulk Au electrodes in acetonitrile and $TBABF_4$ medium had shown that the effects of Au dissolution can be suppressed by the rapid formation of a polymer monolayer on the electrode surface. In fact, as our results indicate, this effect may occur just during the first cycles. After the initial cycles, the adsorption of critical size oligomeric clusters may predominate and a modified electrode surface is produced. That this occurs was verified not only by the disappearance of soluble products after about two cycles but also by the blue layer, which was formed on the top of the PMT films obtained at a more negative final potential.

The electropolymerization of 3-methylthiophene on Au was also investigated by applying constant potentials of 1.50, 1.55, and 1.60 V. Although potentials as high as 1.55 V were shown to be sufficiently high to promote the film growth, in some cases a low current or no current was obtained, probably because the predominant effect was the Au dissolution. Furthermore, soluble products were formed in most of these experiments. These results lead to the conclusion that in order to produce PMT films by potential steps, it is necessary to change either the working electrode or the electrolyte salt.

Monomer Concentration. We varied the monomer concentration in order to verify whether the anodic dissolution of Au was concurrent with the monomer oxidation. From Figure 2a, one notices that the current density at peak A is smaller at a higher monomer concentration. For the following cycles shown in Figure 2b, the current density increases with the number of cycles (see arrow) even upon decreasing the value of E_f to 1.6 V after the first cycle.

The effect of increasing the monomer concentration on the early growth stages of polythiophene films was previously reported[19] using Pt electrodes in CH_2Cl_2 media and different electrolyte salts. It was verified that higher monomer concentrations promote a progressive growth of nuclei in opposition to an instantaneous nucleation mechanism. Furthermore, a higher rate of formation of oligomers at the electrode/solution interface justifies why thicker films are commonly obtained at higher monomer concentrations. However, the increase of the current density with the number of cycles does not necessarily yield thicker films, since polymer films may deposit on the electrode surface by different processes of nuclei coalescence upon varying the monomer concentration, electrolyte nature, and potential range as was previously reported for thiophene.[19]

Electrode Treatment. The voltammetric response of Au-coated electrodes pretreated with different etch solutions was also studied. No visible modification of the Au surface was observed after the pretreatments, except for those electrodes immersed for long times in aqua regia solution. Creager et al.[13] have shown that even dilute aqua regia solutions ($HCl/HNO_3/H_2O$ 3:1:6) etch the Au layer

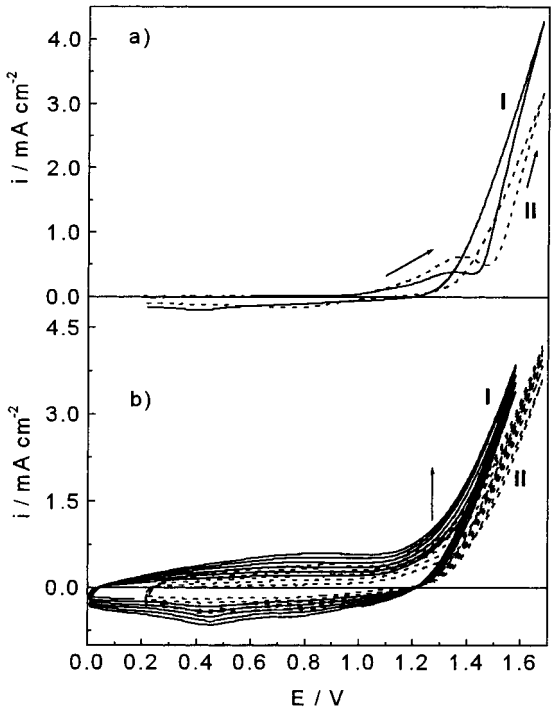

Figure 2. Cyclic voltammograms of Au-coated electrodes in acetonitrile medium containing 0.1 mol L^{-1} (curves I) and 0.2 mol L^{-1} (curves II) 3-methylthiophene and 0.1 mol L^{-1} $TBABF_4$: (a) first cycle; (b) successive cycles; v = 20 mV s^{-1}.

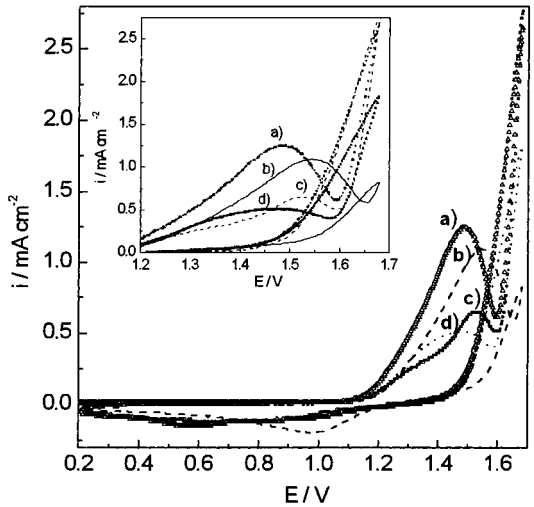

Figure 3. Cyclic voltammograms of Au-coated electrodes in acetonitrile medium containing 0.1 mol L^{-1} 3-methylthiophene and 0.1 mol L^{-1} $TBABF_4$; v = 20 mV s^{-1}. Electrode treatment: $H_2O/NH_4OH/H_2O_2$ (SC) (5:1:1 v/v) for 5 min (a) and 20 min (b); dilute aqua regia ($HCl/HNO_3/H_2O$ 1:3:10 v/v) for 5 min (c) and 7 min (d).

removing Au (0.49 mg after 5 min of treatment). We noticed that the pretreatment time chosen here (7 min) in dilute aqua regia ($HCl/HNO_3/H_2O$ 3:1:10) was sufficient to expose the Cr underlayer which appeared as randomly distributed, small blue spots. In our studies, surface modifications were not seen on Au electrodes immersed in this solution for less than 5 min.

As can be seen in Figure 3, the surface pretreatment significantly influenced the electrochemical response of the Au electrode in $TBABF_4$ medium. The A peak showed a better definition for electrodes treated in acidic (aqua regia) or basic (SC) etch solutions, which are known to be

(18) Hillman, A. R.; Mallen, E. L. *J. Electroanal. Chem.* **1987**, *220*, 351.

(19) Schrebler, R.; Grez, P.; Cury, P.; Veas, C.; Merino, M.; Gómez, H.; Córdova, R.; del Valle, M. A. *J. Electroanal. Chem.* **1997**, *430*, 77.

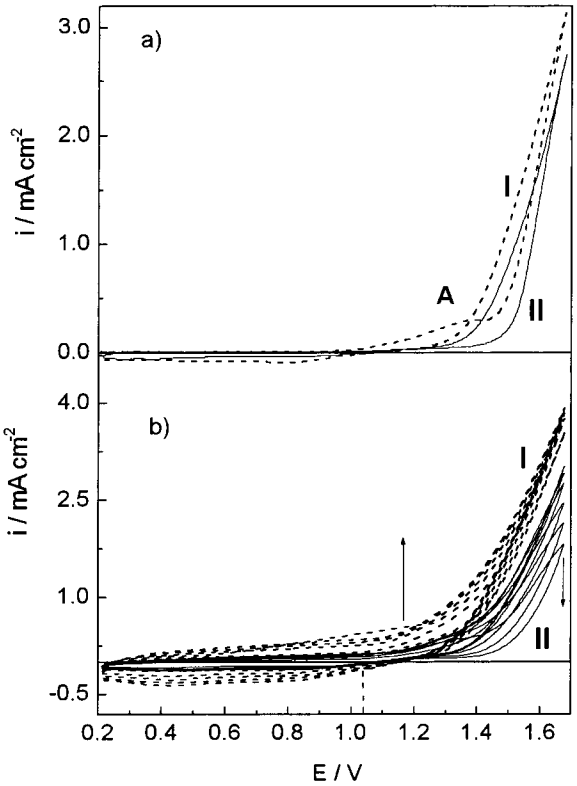

Figure 4. Cyclic voltammograms of Au-coated electrodes in acetonitrile medium containing 0.1 mol L^{-1} 3-methylthiophene and 0.1 mol L^{-1} $TBABF_4$ (curves I) and 0.1 mol L^{-1} $LiClO_4$ (curves II): (a) first cycle; (b) successive cycles; $v = 20$ mV s^{-1}.

capable of eliminating organic layers and particle contaminants from surfaces.[20]

As expected, the PMT film obtained after two cycles on Au treated in aqua regia for 7 min showed darker regions and a blue top layer, which indicated exposure of the Cr underlayer. While the PMT film deposited on the Au electrode etched in aqua regia for 5 min showed no top blue layer and a smooth surface, when Au electrodes treated with SC solution were used, the film obtained was very thin, as expected for the low current noted in the voltammograms due to the oxidation of 3-methylthiophene. In particular, a bluish product formed in solution after several cycles provided strong evidence for the Cr underlayer exposure from electrodes treated in aqua regia.

Electrolyte Salt. As shown in Figure 4, the A peak was not observed for solutions containing $LiClO_4$ but rather was observed only for $TBABF_4$. Therefore, the electrolyte salt is the most relevant parameter related to the anodic dissolution of Au. Another interesting observation is the decrease of the current density with the number of cycles in the $LiClO_4$ medium as compared with $TBABF_4$ (see arrows). Although it is not seen in this figure, the current density for voltammograms in the $LiClO_4$ medium increases up to the second cycle, and then it decreases monotonically with the number of cycles.

If we consider that the increase of the current density with the successive cycling is related to a continuous increase of the film thickness, then the use of $TBABF_4$ provides a more efficient process of film deposition. Thus, it is noteworthy that adherent and homogeneous PMT films are obtained in $TBABF_4$ after only two cycles, even though Au undergoes anodic dissolution before a potential high enough to oxidize the monomer is reached. A more efficient deposition process of polythiophene films on a Pt electrode has been observed in a medium of CH_2Cl_2, thiophene, and $TEABF_4$ (tetraethylammonium tetrafluoroborate) as compared with $TEAClO_4$.[19] This difference has been related to differences of solubility of oligomers formed in these two media. This topic is currently being investigated in our laboratory.

Adsorption Processes. The nucleation and growth steps of a polymer film on the electrode surface may differ according to variables such as final potential, monomer concentration, electrolyte, and electrode nature/treatment. Two possible processes for polymer growth can be proposed from monomers such as aniline, pyrrole, and thiophene and derivatives (early growth stages):[21,22] (i) adsorption of the monomer on the electrode surface followed by oxidation and formation of oligomers; (ii) oxidation of the monomer coming from the electrolyte solution and formation of oligomers at the interface electrode/solution followed by adsorption of these oligomers on the electrode surface. This first stage of nucleation depends on the nature and surface characteristics of the electrode and the monomer. The possibility of chemical adsorption of thiophene on Au is a controversial matter. Although previous reports have described well-ordered monolayers of thiophene on Au(111),[23,24] Elfeninat et al.[25] and Lavrich et al.[26] showed that thiophene did not chemically interact with Au as was the case for several other sulfur-containing compounds. One may consider that the chemical adsorption of 3-methylthiophene before its oxidation on the Au electrode surface can be effective in protecting Au against dissolution (without considering desorption effects). However, our experiments indicated that the chemical adsorption of 3-methylthiophene on Au is likely not occurring, at least under the experimental conditions (solvents and immersion times) and using the techniques (cyclic voltammetric and spectroscopic ellipsometry) chosen to verify any surface modification.

Three solutions were tested: 10 mmol L^{-1} 3-methylthiophene in propanol (electrodes immersed for 12 h), *N*-methylpyrrolidone (12 h), and methanol (several days). For these experiments, the Au electrodes were kept in closed containers and immersed in these solutions (solvent and 3-methylthiophene) at room temperature after deoxygenating for 1 h. After these immersion periods (12 h or several days), the Au electrodes were rinsed with copious amounts of solvents and dried with a stream of nitrogen.

To verify adsoption of 3-methylthiophene on the Au surface, we used two techniques, spectroscopic ellipsometry and cyclic voltammetry, which are useful tools to verify adsorption of alkanethiols on coated-Au substrates.[10,13,16,27] The presence of organic monolayers on the electrode surface hinders electron transfer reactions that usually appear in the voltammograms of bare Au electrodes. In addition, from the ellipsometric analysis, psi and delta, the measured ellipsometric parameters, also

(20) Wolf, S.; Tauber, R. N. *Silicon processing for the VLSI era, vol. 1, process technology*, 2nd ed.; Lattice Press: Sunset Beach, CA, 2000; p 129.

(21) Abrantes, L. M.; Correia, J. P. *Electrochim. Acta* **1999**, *44*, 1901.

(22) Kankare, J. In *Electrical and optical polymer systems – fundamentals, methods, and applications*; Wise, D. L., Wnek, G. E., Trantolo, D. J., Cooper, T. M., Gresser, J. D., Eds.; Marcel Dekker: New York, 1993; p 167.

(23) Dishner, M. H.; Taborek, P.; Hemminger, J. C.; Feher, F. J. *Langmuir* **1998**, *14*, 6676.

(24) Dishner, M. H.; Hemminger, J. C.; Feher, F. J. *Langmuir* **1996**, *12*, 6176.

(25) Elfeninat, F.; Fredriksson, C.; Sacher, E.; Selmani, A. *J. Chem. Phys.* **1995**, *102*, 12.

(26) Lavrich, D. J.; Wetterer, S. M.; Bernasek, S. L.; Scoles, G. *J. Phys. Chem. B* **1998**, *102*, 3456.

(27) Finklea, H. O.; Avery, S.; Lynch, M.; Furtsch, T. *Langmuir* **1987**, *3*, 409.

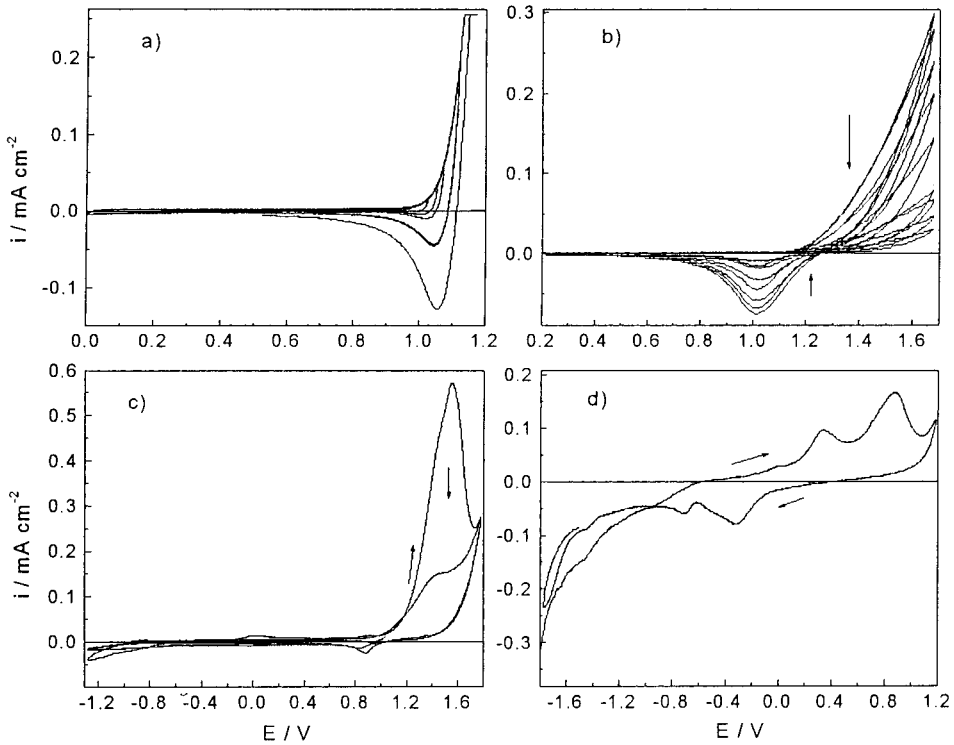

Figure 5. Cyclic voltammograms of Au-coated electrodes in acetonitrile medium containing 0.1 mol L^{-1} $TBABF_4$ (a−c) and after adding 2−3 vol % of water (d); $v = 20$ mV s^{-1}.

change for modified electrodes. Liedberg et al.,[16] for example, reported a decrease of about 95% of the delta values after recovering Au substrates with a functionalized terthiophene. However, we verified here that the ellipsometry results were virtually the same after immersing the Au substrates in the 3-methylthiophene solutions. In addition, cyclic voltammetry did not indicate chemisorption of 3-methylthiophene on the Au surface since the A peak, which corresponds to the oxidation of the bare Au, was clearly seen in the voltammograms of Au upon cycling the potential between 0.2 and 1.7 V in acetonitrile containing $TBABF_4$ and 3-methylthiophene.

Bare Au Electrodes in the Monomer-Free Solution. One of our concerns, which is reported by Skompska,[8] was to be sure that the A peak corresponds to the oxidation of Au to the Au(I) species rather than to the formation of Au oxide due to the presence of traces of water in the electrolyte solution, in particular $TBABF_4$. Wagner and Gerischer[28] attributed the formation and reduction of an oxide layer on Au electrodes to the presence of water in the acetonitrile solvent. Thus, two processes can be distinguished.[28] One process involves the oxidation of Au to AuO_x species in the solvent with a relatively large amount of water (at a minimum concentration of 0.1 vol % H_2O). The other process involves Au dissolution in the dry solvent (0.001 vol % H_2O) at more positive potentials.

To determine the effect of adding water in the electrolyte solution on the voltammetric response of Au, a series of experiments was performed using bare Au-coated electrodes in $TBABF_4$ and $LiClO_4$ solutions. In Figure 5 are shown the cyclic voltammograms of Au in a monomer-free solution containing $TBABF_4$ at different potential ranges (curves a−c) and after adding water (2−3 vol %) (curve d).

No visual modification of the Au surface was noted using a potential range between 0.2 and 1.1 V in the absence of water, which indicates a stable electrochemical response (Figure 5a). However, the surface became bluish after holding a potential of 1.1 V for several seconds. In this case, as the potential scan is continued, the current decreased monotonically with the number of cycles as can be better noticed at a final potential of 1.7 V (Figure 5b). Also, note that in Figure 5c the potential range was extended from −1.0 to +1.8 V causing faster Au dissolution. This potential range allowed the verification of the absence of cathodic peaks associated with reduction of Au oxide after oxidation of water to AuO_x species and protons. The cathodic peak seen in these voltammograms can be attributed to a Au(I) complex species. The voltammetric response of Au in the $TBABF_4$ medium also containing water (Figure 5d) is similar to that obtained in aqueous acidic media by different authors and summarized by Cahan et al.[29]

The removal of the Au overlayer at positive potentials occurred in $TBABF_4$ independent of the thickness of the Au and Cr layers. In this case, we tested an electrode with 1000 Å of Au and 100 Å of Cr, which after successive cycling becomes transparent due to a partial removal of Au. Electrodes without Cr or with only a thinner layer of Cr were not suitable for storage, since they did not resist delamination in solution (the Au films were easily removed from the glass plates using adhesive tape). For the case of using a thinner Cr underlayer, the solution becomes yellow instead of blue after successive cycling in a medium of $TBABF_4$ from 0.0 to 1.7 V.

The absence of an anodic current in the voltammograms of Au in dry acetonitrile and $LiClO_4$ (Figure 6) reinforces our previous conclusions. The presence of traces of water in acetonitrile containing $LiClO_4$ initiates passivation of the electrode, since no visible surface modification was noted after successive cycling of Au in the dry $LiClO_4$ medium.

(28) Wagner, D.; Gerischer, H. *J. Electroanal. Chem.* **1989**, *258*, 127.

(29) Cahan, B. D.; Villullas, H. M.; Yeager, E. B. *J. Electroanal. Chem.* **1991**, *306*, 213.

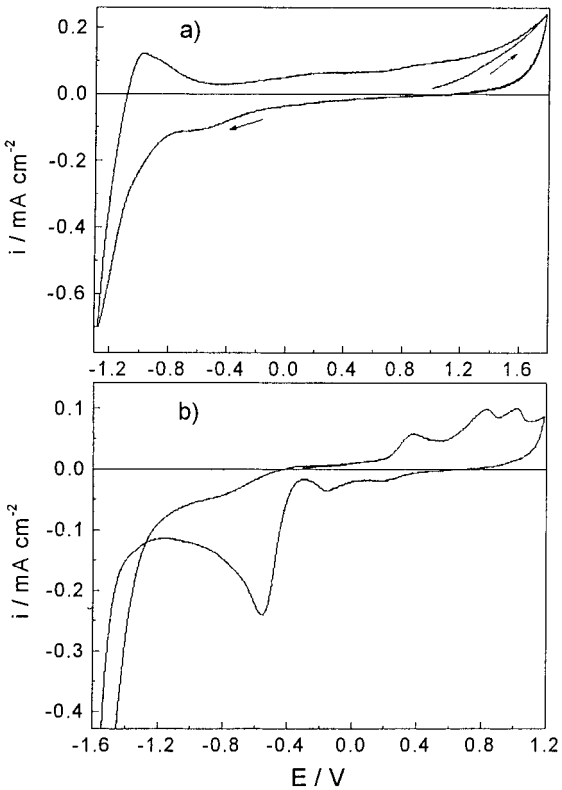

Figure 6. Cyclic voltammograms of Au-coated electrodes in acetonitrile medium containing 0.1 mol L^{-1} $LiCl_4$ (a) and after adding 2−3 vol % of water (b); v = 20 mV s^{-1}.

X-ray Photoelectron Spectroscopy. The XPS results corroborate the conclusions about Au dissolution. Figure 7 shows a comparison of the spectra of Au electrodes before and after successive cycling from 0 to 1.7 V in a monomer-free solution containing $TBABF_4$. This procedure allowed us to obtain a nonuniform blue film that displays a Cr2p peak in the XPS spectra. The signals of the Au4f peak are less intense for the blue film, and a small shoulder appears at 86.5 eV possibly due to Au oxide. Some differences in these spectra as compared to those of Au samples exposed to UV/ozone[30,31] are related to possible impurities present in our samples, which were only cleaned with isopropyl alcohol.

Using XPS, we also verified that the removal of Au during the electropolymerization of 3-methylthiophene was not sufficient to expose the Cr underlayer (Figure 8). The two PMT films chosen for this XPS analysis were those obtained at different values of E_f from Figure 1. No significant variation of the Au surface was noticed by XPS; the spectrum of the yellow, thinner film (sample I) displays more intense substrate signals (with no significant change in the shape of the Au4f peak) and a less intense $S2p_{3/2}$ signal. The XPS spectra did not show new peaks related to different polymer structures or a modified substrate. Furthermore, the Cr2p peak was not detected for either sample, which is evidence that the Au dissolution in fact occurs, but it is suppressed by deposition of a film on the electrode surface.

Presence of Ions. In fact, if Au dissolution occurs in a medium with $TBABF_4$ rather than with $LiClO_4$, then how can one explain the results in a medium of 3-dodecylthiophene and $LiClO_4$ reported by Skompska?[8] At first, we related the unexpected anodic dissolution of Au in

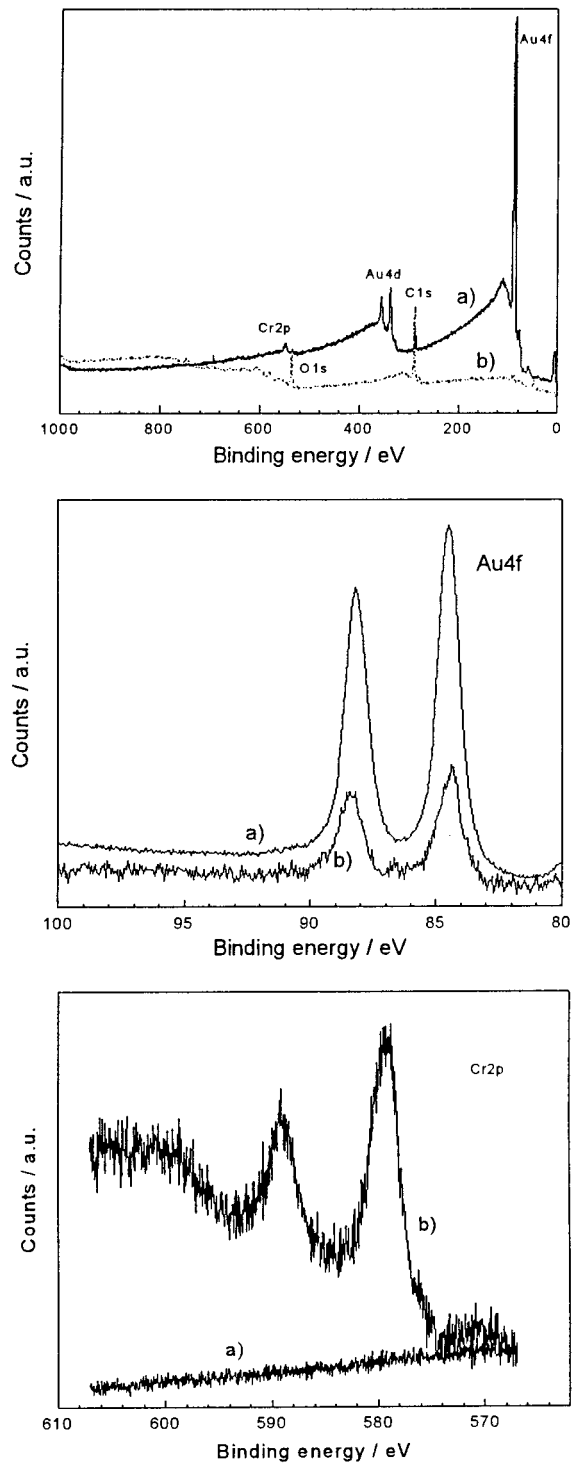

Figure 7. XPS spectra of Au-coated electrodes before (a) and after (b) successive potential cycling in the $TBABF_4$ medium.

$TBABF_4$ to the possible presence of acidic contaminants such as HF which point to the reports of Cahan et al.[29] and Kissner et al.,[32,33] who studied the effect of traces of anionic impurities in the electrolyte solution on the voltammetric response of Au electrodes. In these studies, traces of Cl^- or SO_4^{2-} at about $(2-3) \times 10^{-6}$ mol L^{-1} added to an aqueous acidic medium[28] ($HClO_4$) or Cl^-, Br^-, and I^- at about $(3-5) \times 10^{-6}$ mol L^{-1} to nonaqueous acetonitrile ($TEAClO_4$, $TBAPF_6$)[29,30] were sufficient to drastically modify the voltammetric response of Au.

Schmid and Curley-Fiorino[34] discussed a phenomenon of Au dissolution on Au-plated Pt foils upon applying a

(30) King, D. E. *J. Vac. Sci. Technol., A* **1995**, *13*, 1247.
(31) Kroger, A.; Rodahl, M. *J. Vac. Sci. Technol., A* **1997**, *15*, 1704.

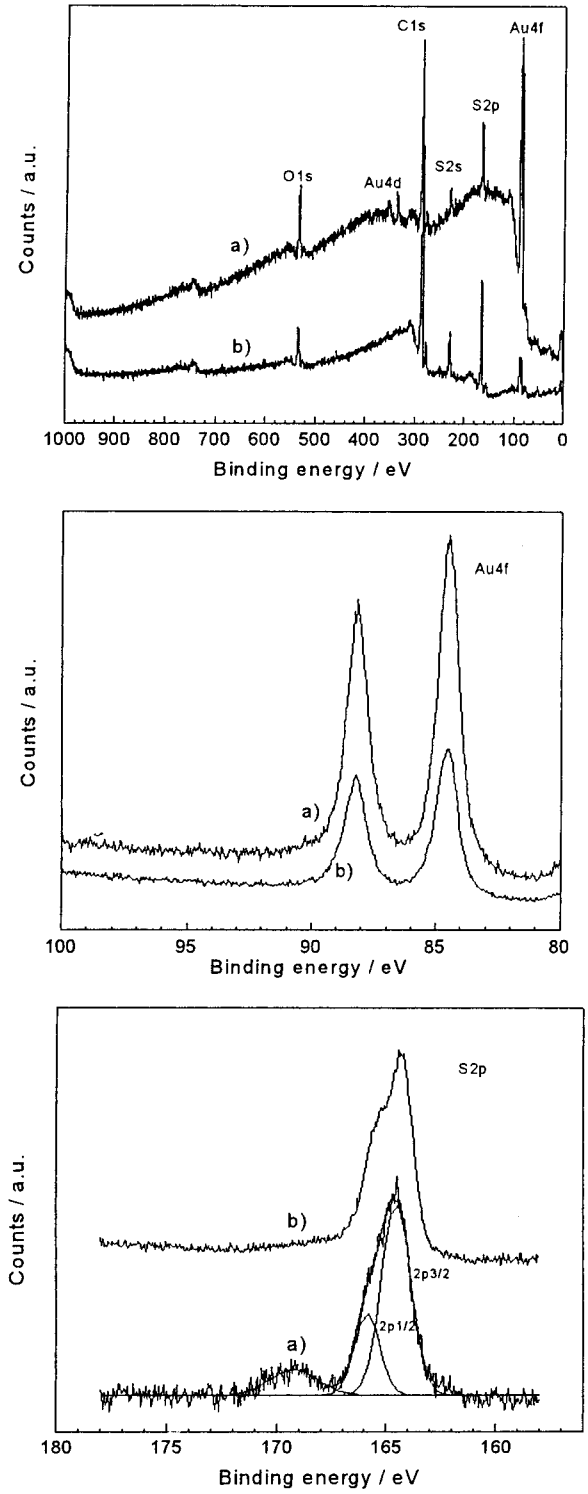

Figure 8. XPS spectra of PMT films prepared at different potential ranges according to Figure 1: (a) experiment I; (b) experiment II.

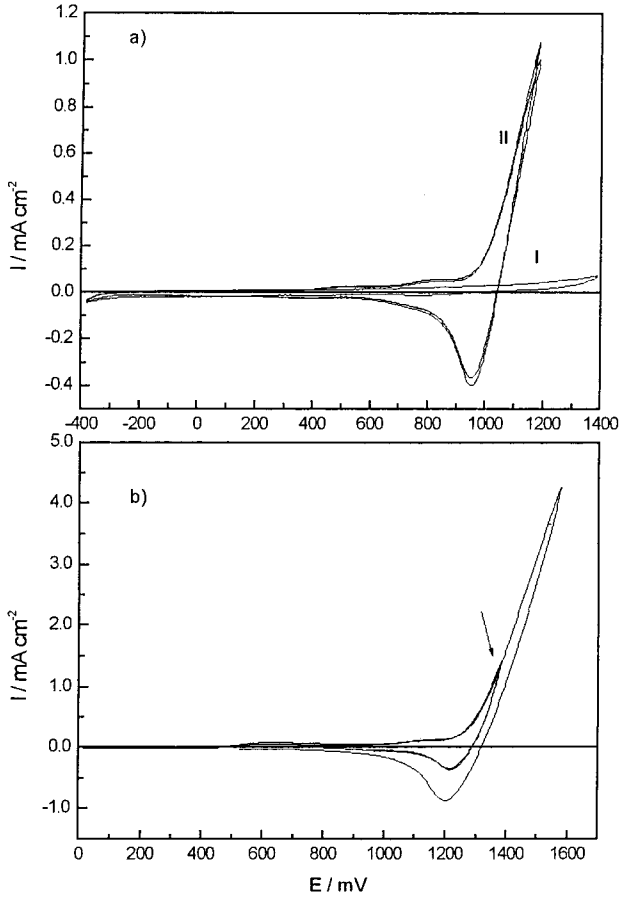

Figure 9. Cyclic voltammograms of Au-coated electrodes in acetonitrile medium containing (a) 0.1 mol L^{-1} $LiClO_4$ and (b) 0.1 mol L^{-1} $TBABF_4$ and 3×10^{-7} mol L^{-1} NaF (curves I) and THACl (curves II); $v = 20$ mV s^{-1}.

constant value of potential in acetonitrile solutions after adding chloride ions to the electrolyte solution ($TEAClO_4$ in acetonitrile). For this case, a complex species, $[AuCl_2]^-$, was proposed to be formed. In another study specifically concerned with Au complexes,[35] the anodic dissolution of Au(0) from a Au layer/platinum electrode was reported to occur in a medium of CH_2Cl_2/$TBAPF_6$ only after intentionally adding an excess of Cl^-. Thus, for the interpretation of our voltammetric results of Au in $TBABF_4$, there is a strong possibility that Au dissolves due to the presence of traces of impurities in the electrolyte solution prepared from the commercially obtained salt. To verify this hypothesis, we followed a sequence of experiments. First, we used a plastic cell to avoid contaminations from the possible chemical attack of $TBABF_4$ on the glass cell. A similar effect of Au dissolution was found using the plastic cell, evidencing that the presence of traces of impurities cannot be attributed to dissolved glass. We also verified a dissolution effect of Au using a sample of recrystallized $TBABF_4$ salt from another laboratory. The next step was to add small amounts of different salts to the electrolyte solution. As noticed in Figure 9, the dissolution of Au is accelerated if tetrahexylammonium chloride (THACl) is intentionally added to the electrolyte solution (0.1 mol L^{-1} $LiClO_4$, curves a-II, and 0.1 mol L^{-1} $TBABF_4$, curves b). No voltammetric modification was observed for Au in a medium of NaF solution, also presented for the sake of comparison. The marked increase of the current density and a blue appearance of the electrode after several cycles evidenced a fast dissolution of Au in the presence of Cl^-.

Finally, two $TBABF_4$ samples (ours and the other recrystallized sample used) were analyzed (Galbraith Laboratories, Knoxville, TN). Results of elemental analysis indicated traces of Cl (47 and 173 ppm, respectively) and

(32) Kissner, R. *J. Electroanal. Chem.* **1995**, *385*, 71.
(33) Kissner, R.; Latal, P.; Geier, G. *J. Chem. Soc., Chem. Commun.* **1993**, 136.
(34) Schmid, G. M.; Curley-Fiorino, M. E. In *Encyclopedia of Electrochemistry of the Elements*; Bard, E. J., Ed.; Marcel Dekker: New York, 1975; Chapter IV-3, p 87.
(35) Koelle, U.; Laguna, A. *Inorg. Chem. Acta* **1999**, *290*, 44.

extremely high levels of S as interferences in both salts. From all these results, we can conclude that either Cl^- or SO_4^{2-} can be considered as responsible for an unexpected effect of Au dissolution in $TBABF_4$ or other salts such as $LiClO_4$ possibly from starting materials used to synthesize these salts.

Conclusions

The anodic dissolution of Au-coated electrodes was found to yield a well-defined anodic peak during the electropolymerization of 3-methylthiophene in acetonitrile and $TBABF_4$ medium. The current density at this peak showed a strong dependence on the monomer concentration and surface treatment. However, Au dissolution was not observed using another electrolyte salt, $LiClO_4$, which allowed us to hypothesize that Au dissolution occurred due to the presence of unexpected contaminants such as chloride in the $TBABF_4$. Possible influences of traces of water in the electrolyte solution were negated after using acetonitrile containing a certain amount of water. Although the exposure of the Cr underlayer was noted upon cycling the electrode at lower final potentials in $TBABF_4$, the XPS spectra of PMT films did not show the Cr signals. Therefore, the Au dissolution occurs during the early stages of polymer film growth, but it is not significantly high enough to cause loss of the Au overlayer under controlled synthesis conditions.

Acknowledgment. D.G. acknowledges the Brazilian agency FAPESP for a fellowship. The authors acknowledge the National Science Foundation (NSF) for support. The authors thank Dr. Natalya Suvorova for her assistance with the XPS measurements.

LA0101090