Growth of Electropolymerized Polyaniline Thin Films

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Electroactive polyaniline films were grown by potentiodynamic electropolymerization at planar gold electrodes from deaerated solutions of aniline (1.0 M) in aqueous HCl (2.0 M). Films were produced by repeated cycling over the range −0.20 to +0.65 V vs SCE to six different levels of electropolymerization charge density. At each level, the separate films were analyzed by cyclic voltammetry at a 50 mV/s scan rate in deaerated 0.2 M HCl at 20 °C, by *ex situ* spectroscopic ellipsometry over the range 1.5–4.0 eV at an incidence angle of 70°and by Rutherford backscattering spectroscopy (RBS) using a ^{4}He ion beam with an energy of about 1.8 MeV. The anodic charge density measured at 50 mV/s over the range −0.20 to +0.80V vs SCE varied from 8.6×10^{-4} to 1.2×10^{-2} C/cm^2. Measured film thicknesses, determined by spectroscopic ellipsometry, varied from 100 to 1600 Å. The anodic charge density was found to correlate linearly with film thickness over this range, consistent with surface confined electroactivity. The molar concentration of oxidizable equivalents in the polymer film is a remarkably constant 4.3×10^{-3} M equiv/cm^3 over the thickness range studied. RBS analysis of the polymer film indicates that within the limit of the depth resolution of the RBS instrument the Cl species are evenly distributed throughout the thickness of the film and that these species include both polymer cation associated chloride ion and trapped HCl.

Introduction

Polyaniline (PAN), its redox state variants, and its aryl-substituted derivatives have attracted considerable new attention, for both scientific interest and commercial application, since the recent report of its electropolymerization at an inert electrode.[1] The attention is justified by the relative ease with which this polymer and its copolymers may be chemically[2,3] or electrochemically synthesized,[1,4] its excellent environmental chemical stability,[5,6] the reversibility of the redox reactions,[7,8] and the very large and dramatic change in electrical conductivity that occurs upon simple oxidation and reduction.[6,8,9] The commercial appeal is found in the use of electroactive polymers, such as polyaniline, as chemoresistive transducers[10] and as redox mediators[11] in various forms of chemical sensor devices and as voltage-stimulated reservoirs for the controlled release[12] or concentration[13] of anionic but electroinactive species.

Electropolymerization offers the capability to grow these films by precise control of the electropolymerization charge, to direct the film to targeted conducting or semiconducting sites of complex device structures[10,14] and to achieve composition and materials property control by electrophoretic blending with other non-redox-active polymers.[10,15–17] Two approaches are possible for the electropolymerization of electroactive polymers while under potential control—the potentiostatic[18] method and the potentiodynamic method.[19–21] Both methods produce the growth of polymer films by the initiation and discharge of redox active monomer at a conductor or semiconductor/solution interface. In the potentiodynamic method, the film is grown by repeated cycling over a potential range selected to induce charge-transfer initiation of the mono-

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mer, growth, and deposition of the polymer film, as well as repeated oxidation and reduction of the electropolymerized polymer. In the potentiostatic method, the film is grown at a fixed potential selected to induce charge transfer initiation of the monomer as well as growth and deposition of the polymer film. However, since the polymer generally has an oxidation potential that is lower than that of its monomer, the polymer is consequently grown under continuously oxidizing conditions.

Paul et al.[8] have measured the thickness of potentiostatically (+0.90 V vs SCE) electropolymerized PAn films using SEM and surface profilometry. The films studied ranged from 0.25 to 26.5 μm and were found to correlate poorly with the electropolymerization charge as well as with the anodic charge density measured by cyclic voltammetry. Stillwell and Park[22] have also measured the thickness of PAn films, and for films of micron thicknesses they have provided the following relationship: T (μm) = $(7.2 \pm 1.5)Q_a$ (C/cm^2) − (0.08 ± 0.16). Wei et al.[23] have measured the mass of potentiodynamically (−0.20 to 0.80 V vs SCE) electropolymerized PAn and found this to be linear with the anodic peak current of the first redox reaction, i_{pa1} (E_{pa1} = ca. 0.17 V vs SCE), up to a peak current density of 12 mA/cm^2. Possible variation in density perpendicular to the plane of polymer film growth limits the value of the mass/current relationship. Furthermore, for chemosensor and biosensor applications of these polymer films, it is the thickness that must be controlled.

In this paper we report on our investigation of the relationship between the electrochemically determined anodic charge density and the thickness of electropolymerized polyaniline films as measured by spectroscopic ellipsometry. We confirm a relationship of the form provided by Stillwell and Park:[22] T (Å) = $1.39 \times 10^5 Q_a$ (C/cm^2) − 34.32, measured over the range 100–1600 Å. Using the measured film thickness, we have determined the molar concentration of electroactive moieties within the electropolymerized polymer film and have found this to be a constant 4.3×10^{-3} M equiv/cm^3 over the range of film thicknesses studied. Rutherford backscattering spectroscopy (RBS) has been used to characterize the distribution of chloride species within the PAn films. This information in turn has been used to characterize the distribution of the electroactive moieties within the polymer film. The distribution of chloride species suggests a uniform electroactivity throughout the PAn film; although thicker films possess more chloride than thinner films. This we believe to be the result of HCl entrapment within the polymer. XPS analysis supports the presence of molecularly bonded chloride within thicker PAn films.

Experimental Section

Instrumentation. Electropolymerization of aniline and cyclic voltammetric characterization of polyaniline films were carried out using an EG&G PAR 173 Potentiostat/Galvanostat outfitted with a PAR 179 digital coulometer. Where needed, potentiodynamic sweeps were accomplished by interfacing the PAR 173 to a PAR 175 universal programmer. Cyclic voltammograms were recorded on an Esterline Angus *XYY′* 540 recorder. Spectroscopic ellipsometry was performed on a custom-designed unit[24] consisting of a Xe arc source, rotating (12.5 Hz) polarizer, sample stage, fixed analyzer, a single prism spectrometer, and a cooled (−15 °C) optical multichannel analyzer as detector.

Materials. Aniline ($C_6H_5NH_2$) was supplied by Aldrich and used after distillation under reduced nitrogen pressure. Acetone, 2-propanol, and Omnisolve triply distilled water were used as supplied. Phosphate buffered potassium chloride, pH 7.2 buffer solution, was prepared in the standard way.[25] Pt foil electrodes were fabricated in these laboratories, and saturated calomel electrodes (SCE) were supplied by Fisher. Electropolymerization of PAn was done on planar gold electrodes (PGE, Model AU-118, AAI-ABTECH). The PGEs are suitable for a variety of characterizations of polymer thin films. The PGE is fabricated from 800 Å of magnetron sputtered gold over 200 Å of adhesion promoting chromium on a chemically resistant, electronics quality Schott D263 Borosilicate glass substrate. The total analytical area of the AU-118 device was 1.18 cm^2. For RBS analysis, different Cr/Au thickness values and substrate materials were found to be more convenient, so for these measurements polymer films were electropolymerized on gold-coated silicon wafers using 1800 Å of gold with 90 Å of chromium as the adhesion promoter. RBS spectral simulation prior to actual measurements showed that when a low-energy (<2.0 MeV) ion beam is used, such a sample configuration will simplify the spectrum by separating the Cr peak from the Cl peak, which is of primary interest in our analysis.

Procedures. The planar gold electrodes were cleaned in a Branson 1200 ultrasonic cleaner by sequential washing—first in acetone, followed by 2-propanol, and finally Omnisolve water. The chemically cleaned electrode was then made the working electrode in a three-electrode electrochemical cell in which a similarly cleaned Pt foil electrode served as the counter electrode and an SCE served as the reference electrode. Cathodic cleaning of the electrode was then carried out by repeatedly cycling between −1.2 and −2.0 V vs SCE for 8 min in pH 7.2 phosphate-buffered potassium chloride. The electrode was rinsed in Omnisolve water before being placed in the electropolymerization solution.

Potentiodynamic electropolymerization of aniline was carried out by repeatedly sweeping at 50 mV/s over the range −0.20 to +0.65 V vs SCE in deaerated 1.0 M aniline/2.0 M HCl solution. Electropolymerization solutions were maintained at a constant temperature of 20 °C in an EG&G PAR Model K2064 water-jacketed microelectrochemical cell. The constant temperature was produced using a Lauda K-2/R refrigerated constant temperature circulator. Six films were separately electropolymerized, each to increasing amounts of total anodic electropolymerization charge density, Q_e. At the end of each electropolymerization films were removed, rinsed thoroughly in 0.2 M HCl, and characterized by cyclic voltammetry (CV), spectroscopic ellipsometry, and Rutherford backscattering spectroscopy.

CV characterization of electropolymerized polyaniline films was done in deaerated 0.20 M HCl at 20 °C by performing single scans at 50 mV/s over the range −0.20 to +0.80 V vs SCE. The anodic charge density (total anodic charge per unit area), Q_a, measured in this manner was established as a standard method for the characterization of electropolymerized polyaniline films.

Spectroscopic ellipsometry of electropolymerized polyaniline films was performed *ex situ* in air on dry films at an incidence angle of 70°. Ellipsometric measurements were made over the range 1.5–4.0 eV with a resolution of 48 meV at 1.5 eV and 24 meV at 4.0 eV.

Rutherford backscattering spectroscopic analysis of the electropolymerized polyaniline films were conducted *ex situ* using the Cornell University ion beam facility (Department of Materials Science and Engineering). A $^4He^+$ ion beam with energy of 1.83 MeV was used with a normal angle of incidence. Computer simulation of the spectra was performed using RUMP software initially developed by Doolittle.[26]

X-ray photoelectron spectroscopic analysis of the electropolymerized polyaniline films was performed on a modified Hewlett-Packard 5950A ESCA spectrometer using a monochromatized Al Kα radiation source at 1486.6 eV. The base pressure of the analyzer chamber was maintained below 5×10^{-9} Torr during analysis. All spectra were charge compensated by using C_{1s} at

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Table I. Evolution of the Electropolymerization Charge Density Q_e, the Anodic Charge Density Q_a, and the Ratio Q_e/Q_a with Time According to the Current Model

Q_e,[a] C/cm²	CV, Q_a,[b] C/cm²	CC, Q_a,[c] C/cm²	thickness,[d] Å	concn, M equiv/cm³
3.02E–02	8.56E–04	1.10E–03	8.30E+01	1.07E–02
6.03E–02	1.77E–03	2.17E–03	1.85E+02	9.91E–03
1.01E–01	2.43E–03	2.92E–03	2.60E+02	9.69E–03
3.01E–01	4.59E–03	5.31E–03	5.70E+02	8.34E–03
6.01E–01	7.73E–03	8.50E–03	1.16E+03	6.90E–03
1.00E+00	1.22E–02	1.32E–02	1.60E+03	7.87E–03

[a] Electropolymerization charge density. [b] Anodic charge density as measured by cyclic voltammetry. [c] Anodic charge density as measured by chronocoulommetry. [d] Film thickness as measured by spectroscopic ellipsometry.

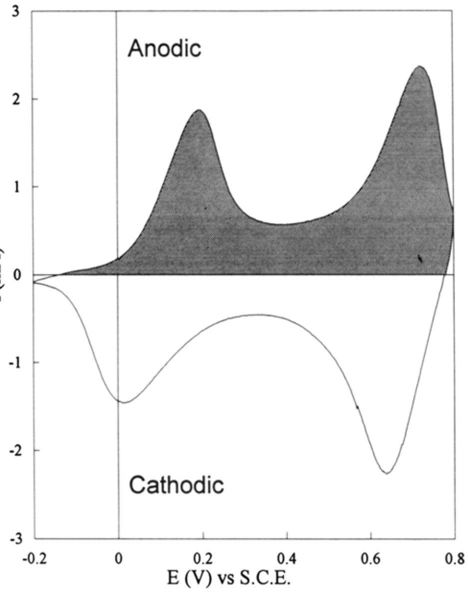

Figure 1. Cyclic voltammogram of an electropolymerized polyaniline film measured over the range –0.20 to +0.80 V vs SCE, at 50 mV/s scan rate in deaerated 0.20 M HCl at 20 °C. The shaded area illustrates the CV anodic charge density, Q_a.

285.0 eV as the energy reference. The spectra were smoothed by the Savitsky–Golay method at a degree of 9.

Results And Discussion

Electropolymerization Kinetics. Cyclic voltammetry (CV) at a 50 mV/s sweep rate over the potential range –0.20 to +0.80 V vs SCE in deaerated 0.2 M HCl was used as a standard method to characterize electropolymerized polyaniline films. The integrated anodic current obtained in a single sweep over this range served to establish the anodic charge density, Q_a, of the film. The anodic charge density, Q_a, obtained by this CV method was compared to the anodic charge density obtained by potential step chronocoulometry (–0.20 to +0.80 V vs SCE). Table I shows the anodic charge density obtained by both these methods in columns 2 and 3, respectively. Since the limiting background current at +0.80 V vs SCE was not insignificant, the chronocoulometric anodic charge was very sensitive to the time base used for current integration and resulted in variations of ca. 20% between these two methods. The CV method was judged more convenient and reproducible and accordingly was used as the standard method. Figure 1 shows a typical cyclic voltammogram of a potentiodynamically electropolymerized polyaniline film obtained under these standard conditions. The characteristic anodic charge density is shown as the shaded area of Figure 1.

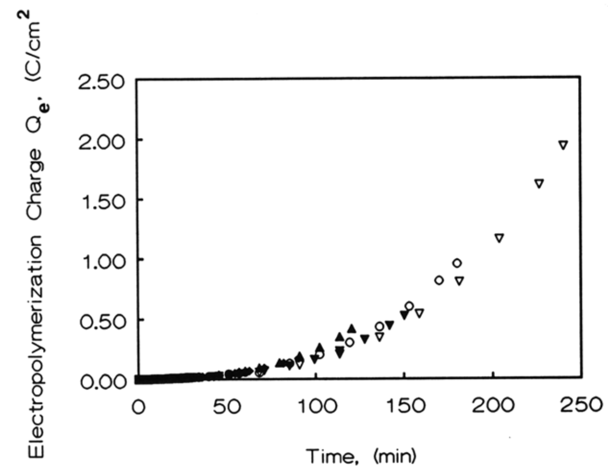

Figure 2. Kinetics of potentiodynamic electropolymerization of polyaniline films as reflected in the electropolymerization charge density, Q_e, monitored over the time course of the polymerization reaction.

Polyaniline films were potentiodynamically electropolymerized to arbitrarily selected but increasing electropolymerization charge. During potentiodynamic electropolymerization of individual films, the anodic current measured during each potential sweep cycle was integrated to yield the anodic electropolymerization charge density, Q_e, in C/cm². After a time sufficient to produce a polyaniline film of approximate desired thickness, there resulted a cumulative electropolymerization charge density, Q_e, that corresponded to the termination of electropolymerization. This value served to characterize the formation of that film. Typical electropolymerization kinetics of individual polyaniline films, reflected in the anodic electropolymerization charge density, Q_e, vs time, is shown in Figure 2. Indeed, a family of such curves is produced for the various PAn films of this study. These polymerization curves show the familiar second-order polynomial growth previously established[4,18,19,23] for the *in situ* electroanalysis of the *continuous* potentiodynamic electropolymerization of aniline. These curves are clustered quite tightly although each reflects the electropolymerization of an individual polyaniline film. The empirical film growth equation is of the form

$$Q_e = At^2 + Bt + C \qquad (1)$$

where Q_e (C/cm²) is the electropolymerization charge density discharged in forming the film. The average variel coefficients obtained were $A = 3.10 \times 10^{-5} \pm 1.30 \times 10^{-5}$, $B = 1.56 \times 10^{-3} \pm 1.59 \times 10^{-3}$, and $C = 2.23 \times 10^{-2} \pm 2.79 \times 10^{-2}$ at 20 °C. The associated correlation coefficient is 0.998. The magnitude of the constants are expected to be functions of such system variables as the concentration of aniline, scan rate, and switching potential.[4] In addition, poor control of electropolymerization temperature greatly increases scatter in the kinetic data. Zotti et al.[4] have found that for the *continuous* electropolymerization of PAn in strong acids such as HCl and H_2SO_4, the electropolymerization charge followed the second power of the cycle number (equivalent to time). These authors inferred from the linear correspondence between the rate of anodic discharge of species (electropolymerization current) and the growth of the polyaniline film (time) that there must also be a corresponding increase in the active surface area of the electropolymerized polymer. The increase in surface area was subsequently[19] attributed to an evolving PAn morphology. Wei et al.[23] have also reported a second-order polynomial growth curve but found that the mass of polymer increased linearly with time.

The observed second-order dependence on time may be adequately explained from a consideration of a potentiodynamic electropolymerization scheme which considers the three general events of initiation, propagation, and electrophoretic deposition as the prime contributors to the growth of electropolymerized polyaniline on an electrode. In this scheme, monomer oxidation, occurring on the leading edge of the oxidation half-wave for aniline, in this case approximately 0.65 V, produces an activated species that is capable of initiating polymerization. This species may be a radical cation as previously suggested by other authors.[27] Electrochemically, only the charge-transfer event leading to formation of the reactive species is accessible from the linear sweep electropolymerization. The reactive species is then the basis for a subsequent coupling or propagation[23,28] reaction leading to polymer formation. Insight into subsequent chemical coupling or propagation events is not generally accessible from the potential sweep experiment. Following propagation, there results a charged species which is *quantitatively* deposited onto the electrode (anode) by electrophoresis and electroendosmosis.[29] Subsequent linear sweep cycles reoxidize the electrodeposited polymer. If the anodic charge density required to promote charge-transfer initiation of aniline monomer is a constant, Q_i, for each potentiodynamic cycle *and* the corresponding anodic charge density of the electrophoretically deposited polymer film is exactly the same as that discharged during initiation, then the following simple relationship will evolve. At the end of cycle 1 the total anodic electropolymerization charge Q_e will be equal to Q_i, corresponding to one initiation pass with no deposited polymer on the electrode. At the end of cycle 2 the anodic electropolymerization charge Q_e will be equal to $3Q_i$, corresponding to two initiation passes plus the charge density of a single, previously deposited polymer film on the electrode. At the end of cycle 3 the anodic electropolymerization charge Q_e will be equal to $6Q_i$, corresponding to three initiation passes plus the charge density of a total of three, previously deposited polymer films on the electrode. The equivalent of three deposited polymer films will contribute on the third pass since all previously deposited polymer films are counted cumulatively in each potentiodynamic sweep. We may define Q_a as the anodic charge density of the electropolymerized polymer film. Q_a, therefore, is the charge content of the electropolymerized film (equivalent to the measured anodic charge density) at some time t (corresponding to the total time for an electropolymerization) measured in the absence of the monomer. This polymer growth scheme produces the evolutionary pattern of results shown in Table II.

This scheme supports that the kinetics of polymer film growth, reflected in the time dependence of the total electropolymerization charge density, Q_e, will be a second-order polynomial as previously indicated. Moreover, the scheme also supports that a plot of the ratio, Q_e/Q_a, versus electropolymerization time will be a straight line. Figure 3 is such a plot of the ratio, Q_e/Q_a, versus the electropolymerization time. This is seen to be a straight line of the form $Q_e/Q_a = 0.39\ t\ (\text{min}) + 0.76$ ($R_{\text{val}} = 0.995$), aptly demonstrating the validity of the scheme. The second-order dependence on time is therefore a consequence of the electropolymerization scheme and is not, under these conditions, fundamental to the mechanism of polymer growth. The single insightful contribution of this scheme to the mechanism of electropolymerization is the observation that, with regard to electroactivity, all of the polyaniline formed by charge-transfer initiation is *quantitatively* deposited onto the electrode and is subsequently available to be reoxidized as PAn. The evolving relationship between Q_e and Q_a suggested by the above scheme would be the same if Q_i were not a constant but changed with each cycle from Q_{i1} for the first cycle through Q_{iN} for the Nth cycle.

Table II. Evolution of Measurable Charge Densities of Potentiodynamically Electropolymerized Polyaniline Films

cycle (time)	Q_a[a]	Q_e[b]	Q_e/Q_a
1	Q_i	Q_i	1
2	$2Q_i$	$3Q_i$	1.5
3	$3Q_i$	$6Q_i$	2
4	$4Q_i$	$10Q_i$	2.5
5	$5Q_i$	$15Q_i$	3
6	$6Q_i$	$21Q_i$	3.5
7	$7Q_i$	$28Q_i$	4

[a] Q_a = anodic charge density of the electropolymerized polymer film. [b] Q_e = cumulative electropolymerization charge density.

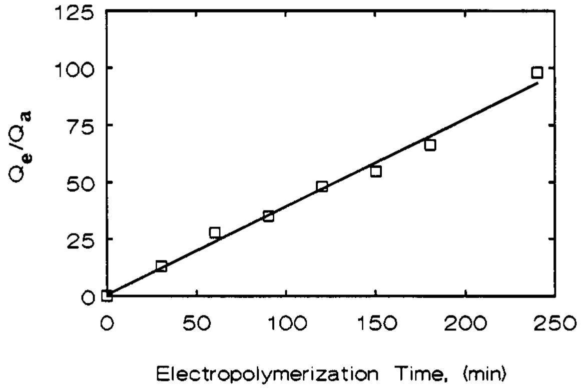

Figure 3. Plot of the ratio of electropolymerization charge density, Q_e, to the anodic charge density, Q_a, versus the electropolymerization time.

These results are consistent with the previously reported observations of others.[4,18,19,23,27c] The positive slope of Figure 3 confirms that the increase in the anodic electropolymerization charge density, Q_e, is faster than the increase in the anodic charge density of the PAn deposited on the electrode, Q_a. The straight line nature of the plot implies quantitative deposition of polymer onto the electrode. This is consistent with a mechanism based on chain-type polymer growth in which the growing polymer film provides new or additional active sites for the charge-transfer initiation of aniline. The amount of aniline initiated in each cycle increases with an increase in the amount of PAn deposited onto the electrode (from previous cycles). Suitable active sites for the preserved electroactivity may be the polymer chain ends, as suggested by Sasaki et al.[30] In this model the number of active sites simply grows with the growth of the polymer film and

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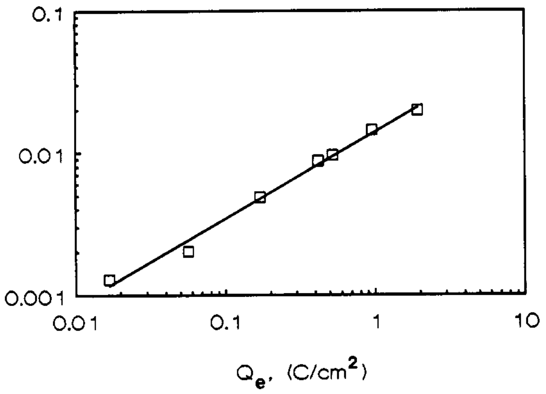

Figure 4. Plot of the electropolymerization charge density, Q_e, versus the anodic charge density, Q_a.

thereby accounts for an increased polymerization rate with time.

Comparison of the anodic charge density of the electropolymerized polymer film (as measured by the above standard cyclic voltammetric method) with the anodic electropolymerization charge density required to grow that particular film is shown in plot of Figure 4. This plot suggests a power law relationship with a correlation coefficient of 0.996 and is given by

$$Q_a\ (\mathrm{C/cm^2}) = 1.4 \times 10^{-2} Q_e^{0.61}\ (\mathrm{C/cm^2}) \qquad (2)$$

In this equation Q_a (C/cm^2) is the anodic charge density of the electropolymerized polyaniline film measured by cyclic voltammetry over the range −0.20 to 0.80 V vs SCE at 50 mV/s, and Q_e (C/cm^2) is the electropolymerization charge density discharged in forming the film by potentiodynamic electropolymerization. This approximate relationship was used to infer the electropolymerization charge required to produce polyaniline films of reproducible anodic charge density. Polyaniline films of selected anodic charge density were potentiodynamically electropolymerized according to eq 2. Following electropolymerization, the electrode was removed form the electropolymerization bath and characterized by cyclic voltammetry and by spectroscopic ellipsometry. Table I shows the anodic electropolymerization charge density discharged in the fabrication of the polyaniline film, Q_e, the anodic charge density of the electroactive polyaniline film, Q_a, and the thickness of the PAn film as determined by spectroscopic ellipsometry. Separately but similarly prepared PAn films were grown to inferred anodic charge density on metallized silicon substrates for RBS and XPS analysis.

PAn Film Thickness. A suitable optical model for the determination of the thickness of electropolymerized PAn films by spectroscopic ellipsometry was found in the three-medium, parallel-layer composite structure: gold/(PAn + void)/air. Figure 5 shows a plot of the PAn film thicknesses derived from the model versus the anodic charge density measured by the CV standard method. From this plot is provided the following empirical relationship (correlation coefficient of 0.995):

$$T(\text{Å}) = 1.39 \times 10^5 Q_a\ (\mathrm{C/cm^2}) - 34.32 \qquad (3)$$

Here T is the film thickness in angstroms as determined

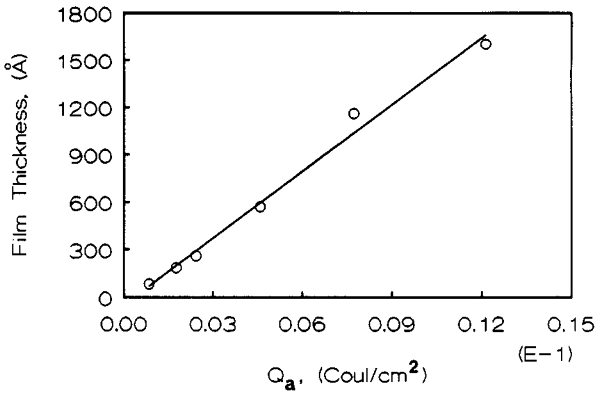

Figure 5. Plot of film thickness, T (Å), as measured by spectroscopic ellipsometry, versus the anodic charge density, Q_a, of potentiodynamically electropolymerized polyaniline films.

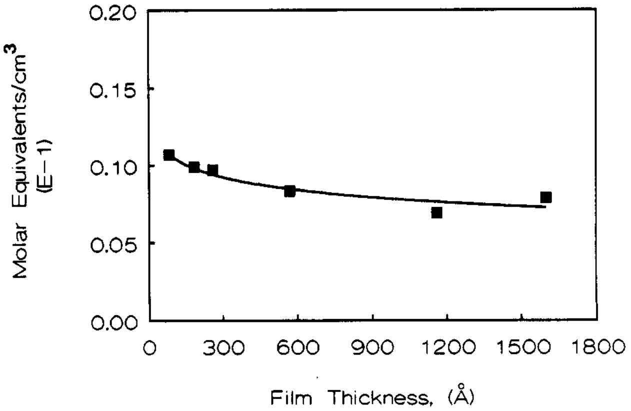

Figure 6. Plot of the molar concentration of electroactive species in potentiodynamically electropolymerized polyaniline films as a function of film thickness.

by spectroscopic ellipsometry and Q_a is the anodic charge density of the polyaniline film in C/cm^2 measured under the standard conditions of 50 mV/s over the range −0.2 to +0.8 V vs SCE. For the low-to-modest film thicknesses used in this work (100–1600 Å), the thickness of the polyaniline films scale linearly with the anodic charge density measured by cyclic voltammetry. This is consistent and characteristic of reversible, surface-confined electroactive species such as immobilized viologen.[31] The thickness of these films measured by spectroscopic ellipsometry are in generally good agreement with those reported by Stillwell and Park[22] and by Paul et al.[8] over the appropriate range. Combining film thickness, charge density, and the application of Faraday's law produces the concentration of electroactive species in molar equivalents per cm^3 for each film. This may be obtained from the slope of Figure 4 or may be calculated for individual data points and plotted as the molar concentration of electroactive moieties in electropolymerized polyaniline films vs thickness as shown in Figure 6. While there is some evolution in molar concentration, this value quickly approaches a limiting value of ca. 8.5 × 10^{-3} M equiv/cm^3 for films which are thicker than ca. 300 Å.

In making the conversion from anodic charge density to molar concentration it is necessary to note that the anodic charge density of each film, as measured by CV at 50 mV/s over the range −0.20 to +0.80 V vs SCE, contains the charge-transfer equivalents for the *two* redox tran-

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sitions evident in pristine polyaniline films. Each of these redox reactions is believed to be a one-electron-transfer reaction as suggested by Huang et al.[32] and Watanabe et al.[28] The total anodic charge density measured by cyclic voltammetry must therefore be divided by two to yield the anodic charge density for the first redox reaction centered on $E^{\circ\prime}$ = 0.1 V vs SCE. The molar concentration calculated in this manner has the limiting value of 4.3×10^{-3} M equiv/cm^3 over the range of film thicknesses studied. It is important to point out that the anodic charge density, Q_a, measured by the present CV standard method, whether *in situ* or *ex situ* to the polymerization solution, is a measure of the concentration of electroactive moieties within the electropolymerized polymer film. The relationship between this value and the concentration of electropolymerized polyaniline formed in the electropolymerization reaction has not been established.

Distribution of the Cl Species from RBS Analysis. Spectral simulations were performed to assist the interpretation of the experimental RBS spectra. The samples were modeled assuming the Si/Cr/Au/PAn structure with sharp layer boundaries and a PAn density of 1.2 g/cm^3. The film thicknesses of Cr and Au were determined during metal deposition and these values stayed fixed in the simulation. Polyaniline film thicknesses obtained from spectroscopic ellipsometry measurements were used as an initial try, and the thickness of the films were then varied in order to obtain the best fit to the experimental data. To determine the thickness of PAn films from RBS spectra, it is necessary to know the correct film density.[33] This density can also be arrived at by taking the weighted average of the elemental densities of the constituent PAn film with the composition being $C_6NH_6Cl_x$. Since the Cr layer is buried deeply, the energy straggle of the He ions can be expected to be a significant factor in analyzing this peak so the Cr peak was corrected for energy straggling.[34]

The experimental RBS spectra of the thickest polyaniline film (1524 Å from SE measurements) is shown in Figure 7 together with simulated spectra for three Cl concentrations with an assumption of uniform Cl distribution throughout the film. Similar spectral simulations were performed on other PAn films with different thicknesses. The general agreement of the simulated with experimental spectra clearly indicates that, within the limit of the depth resolution of the instrument, the Cl species are evenly distributed throughout the thickness of the film. Two extreme cases were also examined using the RBS spectral simulation and are presented in Figure 8 for the thickest PAn film. In one case, the Cl species are assumed to be concentrated in the outermost 300 Å of the film and in the other, in the innermost or bottom 300 Å, i.e., at the polymer/gold interface. The composition of the Cl concentrated layer was assumed to be $C_6NH_6Cl_x$, where x = 0.52. The poor fits of the simulated to experimental spectra clearly excludes the possibility of high surface or interface concentrations of Cl species in the polyaniline films, at least to the extent of the depth resolution of the RBS instrument.

The compositions of the PAn films with different thicknesses based on the RBS spectral simulations are listed in Table III. The film thicknesses derived from the best fit of the RBS spectral simulation are listed also in TableIII together with thicknesses obtained from SE measurements. It should be pointed out that the RBS-derived thickness values might be significantly larger than those listed in Table III, since the film has been assumed to be densely packed in our RBS simulation. It has been

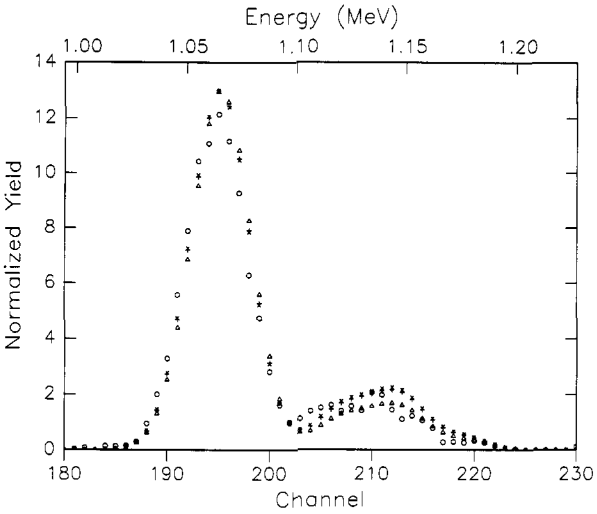

Figure 7. RBS spectrum of a polyaniline film (1524 Å) together with simulated spectra for a uniform Cl distribution throughout the film. The composition of the film was assumed to be $C_6NH_6Cl_x$, where x = 0.50, 0.52, and 0.55, respectively. ○, experimental; △, simulated with [x] = 0.50; +, simulated with [x] = 0.52; ×, simulated with [x] = 0.55.

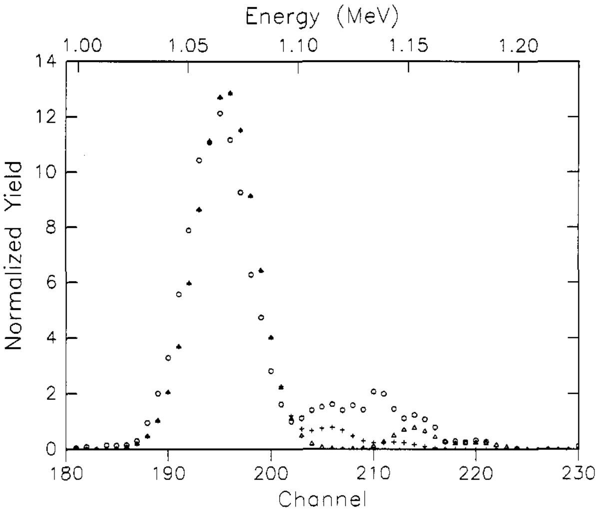

Figure 8. Simulated RBS spectra assuming that the chlorine species are concentrated in the outermost 300 Å and in the bottom 300 Å of the thickest polyaniline film. The composition was assumed to be $C_6NH_6Cl_x$ (x = 0.52) in Cl concentrated layer. ○, experimental; △, simulated with Cl being concentrated on the surface; +, simulated with Cl being concentrated at the interface.

Table III. Compositions of the Polyaniline Films with Different Thicknesses Based on the RBS Spectral Simulations

thickness (nm)		Composition			
SE[a]	RBS[b]	C	H	N	Cl
152.4	150	6	6	1	0.52 ± 0.05
105.6	130	6	6	1	0.45 ± 0.05
79.1	100	6	6	1	0.30 ± 0.05
17.0	40	6	6	1	0.20 ± 0.10

[a] SE: spectroscopic ellipsometry. [b] RBS: Rutherford backscattering spectroscopy.

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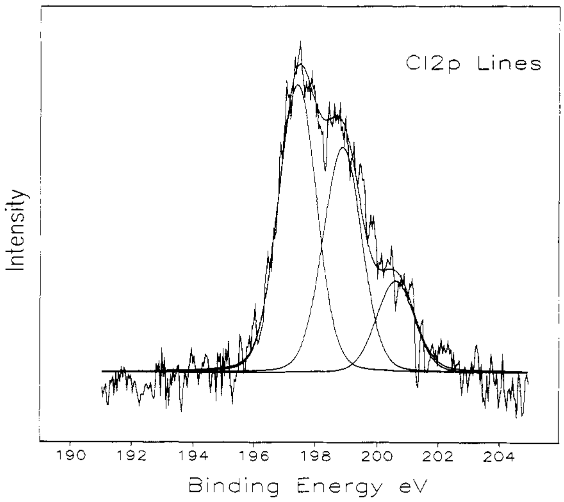

Figure 9. X-ray photoelectron spectrum in the Cl_{2p} region of a 1524-Å polyaniline films.

well-known that polyaniline films obtained from so-called class 2 acid solutions such as H_2SO_4 and HCl tend to be very porous.[19] Finally, Table III also shows the chloride atomic composition inferred from the RBS simulation. There is clearly an increase in chloride content in thicker PAn films.

Polyaniline films prepared by potentiodynamic electropolymerization from 2.0 M HCl and analyzed *ex situ* by RBS following air equilibration are likely the half-oxidized, diprotonated emeraldine·HCl salt. This salt has been reported, based on quantitative ^{13}C NMR analysis,[35] to contain one Cl ion for every two aniline repeat units of the polymer backbone. The measured Cl content in thicker films corresponds well with this expected result. When compared to thinner films, however, it seems to contradict the trend of the concentration of electroactive species shown in Figure 6. It should be realized, however, that due to the insensitivity of backscattering measurements to the nature of chemical bonding, the Cl concentration measured from RBS will include all Cl species. Such species may include chloride ion, as well as covalently bonded chloride. Thus, while the concentration of electroactive moieties within the films remains essentially constant, the total chloride content does appear to increase. In fact, our XPS measurements of the polyaniline films clearly indicates the existence of covalently bonded Cl species in the polyaniline film. Figure 9 shows a typical Cl_{2p} spectrum, in this case obtained from a polyaniline film with a thickness of 1524 Å as measured from spectroscopic ellipsometry. Ideally, if only Cl ionic species existed in the film, one should observe Cl_{2p} spin–orbit splitting doublets with the intensity of the higher binding peak being half of the intensity of the lower binding energy peak. However, exhaustive analysis of the Cl_{2p} spectrum shows that a minimum of three peaks are required to fit the spectrum. The analysis of the spectrum shown in Figure 9 results in the appearance of peaks at the binding energies of 197.4, 198.9, and 200.6 eV. The dominant peak at the lower binding energy of 197.4 eV has been attributed to the contribution from $Cl_{2p_{3/2}}$ originated from Cl atoms associated with alkali metal chlorides.[36,37] The intermediate peak at the binding energy of 198.9 eV can be attributed to the combination of contributions from $Cl_{2p_{1/2}}$ in alkali metal chlorides and from $Cl_{2p_{3/2}}$ in molecular HCl, while the third peak is appropriate for a contribution from $Cl_{2p_{1/2}}$ in HCl.[36] The increased porosity and hence the surface area of the thicker film can certainly increase the possibility of a molecular type of chlorine species, presumably HCl from the electrolyte, being absorbed inside the thicker polyaniline films.

Summary And Conclusions

Potentiodynamic electropolymerization of aniline follows a second-order polynomial dependence upon time. There exists a simple linear relationship between the amount of charge discharged in the potentiodynamic electropolymerization of aniline and the anodic charge density of the electrodeposited polyaniline film. This relationship supports a model for electropolymerization within which monomer initiation and propagation at the electrified interface is followed by quantitative electrophoretic deposition of the electropolymerized polymer onto the electrode. The electrochemical oxidation of electropolymerized polyaniline is a reversible surface confined reaction in which the redox active species are confined within the polymer film. The counter anions required to maintain electroneutrality upon oxidation are drawn from the bulk solution and must gain access by diffusion to redox-active sites within the polymer. The thickness of PAn films, measured by spectroscopic ellipsometry, increases linearly with the anodic charge density of the polymer films. The concentration of electroactive moieties in the polyaniline film therefore, as determined by CV, shows a remarkable constancy with film thickness. For thicknesses over the range 100–1600 Å, RBS analyses support a uniform distribution of chloride species throughout the electropolymerized PAn film. However, while the concentration of electroactive moieties within the polymer film remains essentially constant, there is an increased abundance of chloride species in thicker PAn films. The presence of covalently bonded chloride indicated by XPS suggests that there may be HCl entrapment within the thicker polymer films.

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