

Pulsed-Plasma-Polymerized Aniline Thin Films

Prabhakar A. Tamirisa,¹ KNona C. Liddell,¹ Patrick D. Pedrow,² Mohamed A. Osman²

¹Department of Chemical Engineering, Washington State University, Pullman, Washington 99164

²School of Electrical Engineering and Computer Science, Washington State University, Pullman, Washington 99164

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ABSTRACT: An inductively coupled pulsed-plasma reactor was used to synthesize polyaniline thin films on several substrates positioned at various distances from the center of the radio frequency (RF) coil. The samples were characterized with Fourier transform infrared (FTIR), cyclic voltammetry, and microscopic techniques. Impedance spectroscopy was used to determine the electrical characteristics of three-layer structures with polyaniline as the middle layer between top and bottom metal electrodes. FTIR results indicated that the chemical composition and structure of the films were very dependent on the substrate's position with respect to the RF coil, there being considerably less aromatic character closer to the coil. The electrochemical behavior of the films in acidic electrolytes was similar to that of small-

molecule aniline oxidation products; the number of peaks in the cyclic voltammograms varied with the substrate. Scanning electron microscopy indicated that as the films became thicker, they developed nodules atop a somewhat smoother underlayer. Results from transmission electron microscopy and optical birefringence suggested that the films were not completely homogeneous. The impedance measurements were consistent with relatively rough films possibly containing pinholes. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 1317–1325, 2004

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INTRODUCTION

Plasma polymerization has been used to prepare a wide range of polymer films, including the conducting polymers polyaniline (PAn),^{1–8} polypyrrole,⁴ and polyacetylene.⁹ Among the reported advantages of plasma-polymerized materials are denseness and uniform but controllable film thickness, adhesion and conformability on various substrates,¹⁰ and thermal and chemical inertness.⁵ A wide range of volatile organic compounds can be used as the feed to a plasma reactor, but because no oxidants or solvents are involved, contamination of the film by extraneous species is eliminated in principle,¹¹ and the polymerization process requires only a single step. The composition of a plasma-polymerized film can be tailored with the appropriate processing conditions, and the resulting material properties are often unique and unobtainable by wet synthetic methods.⁵ Although the excited plasma species are mainly high-energy electrons that are relatively indiscriminate in rupturing chemical bonds, the substrate can be kept at the ambient temperature.¹² Overall, plasma polymerization is an inexpensive processing route.

PAn is the most highly conductive of all known polymers and has notably complex structure–property behavior involving four different oxidation states; the

conducting form is stable in both air and water.¹³ The conductivity of plasma-polymerized PAn can be modified by *in situ* doping with iodine vapor;^{3,4,6–8} subsequent ion implantation of I⁺ in PAn films has also been reported.¹⁴ Doping from acidic solutions is well known. The morphology of a PAn film depends on the method of preparation,¹⁵ the substrate,⁷ and the deposition time.⁷ On glass, plasma-polymerized PAn first forms irregular particles, then clusters, and finally a continuous film of irregular pentagons; in contrast, on a Pt substrate, the initial spongy, spherical particles grow into fibrils.⁷ The range of applications for PAn films includes sensors,¹⁶ corrosion protection,^{2,13} and electrochromic displays.¹³

PAn can be synthesized by chemical, electrochemical, or plasma methods, and in each case, the composition, morphology, and physical properties of the resulting polymer are strongly dependent on the detailed reaction conditions. Of particular importance for this study is the fact that the Washington State University (WSU) plasma reactor is inductively coupled and thus differs significantly from capacitively coupled polymerization reactors, in which the reactants may be incident on electrically driven electrodes. Literature values of characteristic reactor parameters were tabulated by Shepsis et al.¹ Compared with pulsed-plasma reactors in other laboratories, the WSU setup provides higher RF power, lower monomer feed consumption rates, a lower ratio of RF on time to RF off time, a longer feed residence time, and higher energy per RF pulse.¹ The pulsed injection of the

Correspondence to: K. C. Liddell.

monomer produces an aerosol, which serves as an economical, quasi-steady-state source of monomer vapor. The molecular structure and physical properties of polymer films prepared under different reaction conditions may be expected to differ.

Among the methods applied to characterize plasma-polymerized aniline are IR spectroscopy,^{2,3,5-8,14,16} ultra-violet-visible (UV-vis) spectroscopy,^{2,8,14} electron spin resonance,² X-ray diffraction,^{3,4} thermal analysis,^{3,4,6} scanning electron microscopy (SEM),^{2,3,6,7,14,15} elemental composition by electron spectroscopy for chemical analysis¹⁵ or X-ray photoelectron spectroscopy,^{2,14} energy-dispersive spectroscopy/scanning electron microscopy,³ and the measurement of various electrical^{2-7,14} and optical properties¹⁴ and the contact angle.^{2,15}

PAn samples prepared by the wet-chemical or electrochemical oxidation of aniline have been examined by a similar range of dry *ex situ* methods. These include IR,¹⁷⁻¹⁹ UV-vis,¹⁸⁻²⁰ X-ray diffraction,¹⁹ SS MAS ¹³C-NMR,¹⁸ SEM,²¹ scanning tunneling microscopy,²¹ and atomic force microscopy.¹⁹ Quantitative and qualitative wet analytical methods have also been applied to these polymers. Methods include gel permeation chromatography,¹⁹ solubility determination,¹⁷ and various electrochemical^{13,20-23} and spectroelectrochemical²³ techniques.

Wet methods have seldom been used in characterizing plasma-polymerized materials. Although it is true that immersing a previously dry polymer film is likely to cause irreversible changes in its properties, invaluable information can be gained that permits a much more detailed comparison of materials made by different process routes. Not surprisingly, a direct comparison of materials made under different conditions is quite difficult.

EXPERIMENTAL

This work extends the earlier use of an inductively coupled pulsed-plasma reactor to prepare polymer films. Independently of the pulsing of the RF plasma, the monomer injector also operates in a pulsed manner; the RF frequency is much greater than that of the injector, so each burst of injected aniline is exposed to a plasma reactor environment that is effectively steady. The pulsed-plasma reactor system has been described thoroughly,^{1,24} but it is worth noting here that the monomer injection system was custom-built and consisted of an automotive fuel injector, a syringe containing liquid monomer under pressure, and an oscilloscope to provide a timing pulse to control the injection of vaporized monomer. When a pulse of the monomer entered the evacuated reactor, most of the liquid immediately vaporized by flash boiling; any remaining liquid disintegrated into droplets that were collected by mesh separators placed about 2 cm from the injector nozzle. In all the experiments reported

here, aniline was injected in 10-ms pulses until the pressure in the reactor reached the desired value; most runs were made at 40 Pa. Because all depositions were performed with a static fill of vapor, electrical pulses used to introduce monomer vapor into the reactor did not have any effect on the final properties of the thin films. One significant equipment modification was made before the experiments reported here. A thermocouple gauge (GIC-11-B, Veeco Instruments, Inc., Woodbury, NY) and capacitance manometer (627A01TBC, MKS Baratron, Andover, MA) were added to the system to improve the monitoring of the reactor pressure. Because capacitance manometers are known to be damaged by a plasma environment, the manometer was used to calibrate the thermocouple gauge in the absence of plasma and then was removed during film deposition; by itself, a thermocouple gauge cannot provide absolute pressures, but it is not affected by the plasma. Calibration runs were performed in triplicate from 0 to 1000 mTorr for air, aniline vapor, and a mixture of aniline vapor and hydrogen.

When enough monomer had been injected into the reactor to reach the desired deposition pressure, the plasma was repetitively activated through the discharge of a 1.8- μ F capacitor initially held at 23 kV, the RF coil excitation being with a damped sinusoid of 290 kHz and a decay time constant of 10 μ s. After 10 such plasma shots, the reactor was evacuated completely and refilled with fresh monomer vapor. One hundred plasma pulses were used to grow most PAn samples. The substrate holder could be positioned at various distances from the RF coil. The substrates included uncoated Si wafers, Si wafers coated with Au or Al, indium tin oxide (ITO) glass, and glass microscope slides; in some runs, the choice of the substrate was dictated by the characterization method that was to be used. The reagent-grade aniline monomer was purified by triple distillation over zinc granules and then stored in a dark bottle under nitrogen.¹³

A profilometer (SPN Technology, Goleta, CA) was used to measure the thickness of representative plasma-polymerized aniline films. The sample morphology and surface uniformity were assessed microscopically with SEM (S-570, Hitachi, San Jose, CA) in the secondary electron mode. Bright-field and diffraction-mode transmission electron microscopy (TEM; 1200EX, JEOL, Peabody, MA) was used to examine thin films mounted with single-stage replication. Optical microscopy was applied to thin films on microscope coverslips with an Olympus BH-2 (Melville, NY) in DIC mode and with a Leitz Orthoplan polarizing microscope.

The chemical characterization of the films was performed with Fourier transform infrared (FTIR) and cyclic voltammetry (CV). Films were grown for FTIR measurements on glass microscope slides and then were scraped off and pressed into KBr pellets. Spectra were recorded between 4000 and 400 cm^{-1} with a

TABLE I
Film Thickness and Average Deposition Rate

Experimental conditions	Thickness (nm)	Average deposition rate (nm/pulse)
13 Pa, 50 plasma pulses	32.78 ± 0.09	0.66 ± 0.09
13 Pa, 100 plasma pulses	98.80 ± 0.05	0.99 ± 0.05
27 Pa, 50 plasma pulses	88.64 ± 0.09	1.77 ± 0.09
27 Pa, 100 plasma pulses	157.5 ± 0.03	1.57 ± 0.03
40 Pa, 50 plasma pulses	236.4 ± 0.04	4.72 ± 0.04
40 Pa, 100 plasma pulses	314.7 ± 0.07	3.15 ± 0.07

PerkinElmer BX FTIR microscope (Shelton, CT); an averaging of 64 scans was done to minimize noise. CV has been widely used to grow PAn films through the electrooxidation of aniline and has provided a wealth of data on the mechanisms of solution synthesis of PAn and related materials. To our knowledge, CV has not been used before to characterize plasma-polymerized aniline, but doing so clearly facilitates a detailed comparison of PAn samples made by wet and dry processes. The experimental setup used an undivided three-electrode cell. All the working electrodes were coated with plasma-polymerized aniline; the substrates included Au vacuum-evaporated onto Si wafers, Pt sputter-coated onto Si wafers, and ITO glass. In each case, a saturated calomel electrode was used as the reference, and the counter electrode was a platinum wire sheathed in a fritted glass tube. A computer-controlled (bi)potentiostat and data acquisition software (Pine Instrument, Grove City, PA) were used.

Electrical properties of plasma-polymerized aniline were studied with impedance spectra of three-layer thin-film structures. These consisted of a conductive bottom electrode (Al, Au, Pt, or C), a PAn layer, and a conductive top electrode (also Al, Au, Pt, or C); the top and bottom electrodes were fabricated by shadow masking, and the PAn layer was grown in the plasma reactor. Impedance data were obtained with an HP 4192ALF impedance analyzer (Hewlett Packard, Palo Alto, CA) operating at a root-mean-square voltage of 0.5 V between 5 Hz and 13 MHz.

RESULTS AND DISCUSSION

Film deposition rate

Variations in the film thickness can provide a direct measure of the net growth rate under different conditions. As Table I indicates, the profilometer data are directly correlated with the pressure in the reactor and the number of plasma pulses, but the growth dynamics are complex. The average growth rate increases with higher pressure for a fixed number of plasma pulses, but at pressures of 27 or 40 Pa, the average rate decreases as the number of pulses is raised from 50 to 100. The drop is more pronounced at higher pressure. At 13 Pa, however, the deposition rate increases if

more pulses are used. Different mechanisms of polymerization or film growth may be rate-controlling under different conditions, and there may be a critical film thickness at which the growth rate slows down.

FTIR characterization of the chemical structure

FTIR spectra (Fig. 1) indicate not only that the chemical bonding in plasma-polymerized aniline differs from that of the monomer but also that the molecular structure of the deposited film is a strong function of distance from the RF coil in the plasma reactor. The strong position dependence of the chemical composition and structure of plasma-polymerized materials has long been known.^{25,26} The films whose spectra are

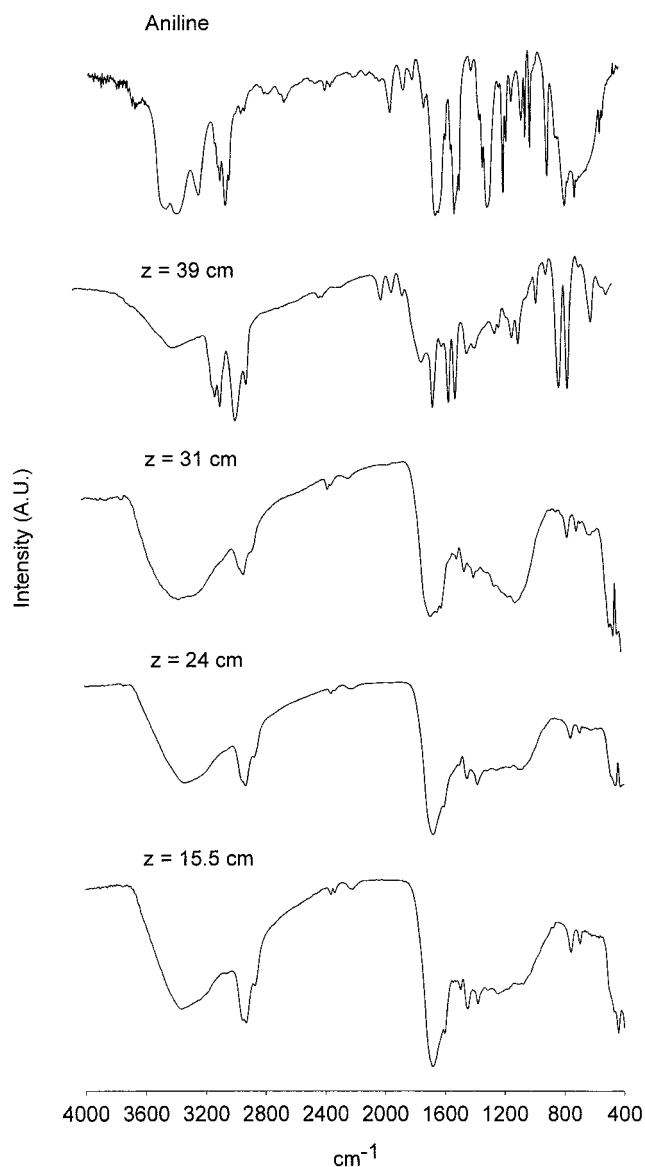


Figure 1 FTIR spectra of aniline monomer and plasma-polymerized aniline films deposited on ITO substrates at various distances from the center of the RF coil. The reactor pressure was 40 Pa, and there were 100 plasma pulses.

TABLE II
FTIR Band Assignments for PAN Deposited 39 cm
from the RF Coil

Wavenumber (cm ⁻¹)	Assignment
3024.04	C—H stretching of aromatic ring
1447.63, 1492.37, 1539.21, 1598.57	C=C stretching of aromatic ring
1027.23, 1069.35, 1182.30, 1155.52	In-plane bending of aromatic C—H
906.29, 841.45 1369.01	Out-of-plane bending of alkene Symmetric deformation of C—H in —CH ₃
1317.53	C—N stretching of aromatic ring
1942.70, 1871.40, 1799.67	Overtone of out-of-plane deformation of aromatic C—H

shown in Figure 1 were grown on glass slides placed 15.5, 24, 31, and 39 cm from the center of the coil, under otherwise identical conditions (40 Pa and 100 plasma pulses). For an easy comparison, the spectrum of the aniline monomer is also shown in Figure 1, but it should be noted that the intensities of all five spectra are in arbitrary units and therefore are not directly comparable. We can determine the effect of the axial position on the chemical functionality of the films by first identifying bands that are common to all four of the PAN spectra and then focusing on features that are significantly different. Common bands include those near 3338 cm⁻¹, indicative of a secondary amine; those at 756 and 698 cm⁻¹, indicative of deformation in a monosubstituted benzene ring; and those at 541 and 439 cm⁻¹, indicative of deformation of a substituted benzene. However, the spectrum for the 39-cm film shows clearer evidence for aromaticity than any of the others. A detailed band assignment for this film is given in Table II. The band at 3024 cm⁻¹ is unique to this spectrum and is assigned to C—H stretching in an aromatic ring. Bands near 1448, 1492, 1539, 1599, 1027, 1069, 1182, and 1156 cm⁻¹ are present in the spectra for the other films but are considerably sharper for the 39-cm film; all are consistent with aromaticity. In addition, bands at 1943, 1871, and 1800 cm⁻¹ have been assigned to overtones of C—H deformations in aromatic rings. Spectra for films grown closer to the RF coil have a prominent band in the region from 1684 to 1673 cm⁻¹, frequencies that are associated with C=O stretching of a ketone. The relative intensity of this band decreases as the axial distance increases, and this suggests that films grown furthest from the RF coil exhibit the highest retention of monomer functionality. These observations are consistent with others of the plasma polymerization of aniline^{2,6-8} and fluorinated monomers.^{25,26} It is believed that free radicals are trapped in the as-grown film in concentrations that increase with the field strength; it is not clear whether these highly energetic species react *in situ* with residual oxygen left in the reactor after pumpdown or whether subsequent exposure to atmospheric concen-

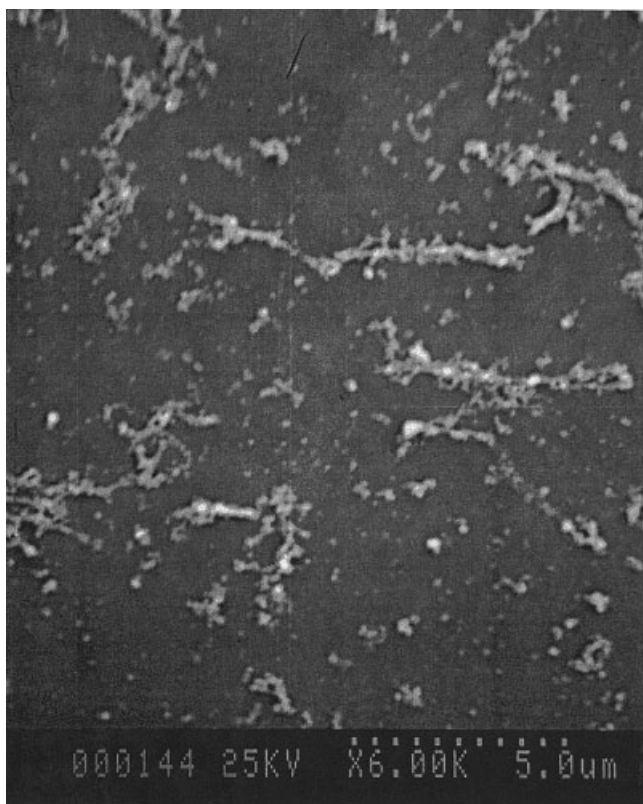
trations of oxygen is required. It may be relevant that films handled in the same way but grown at 39 cm do not show the carbonyl band. The model of electron temperature profiles developed earlier by Shepsis²⁴ predicts that the plasma electrons should be most energetic in the vicinity of the RF coil and that their temperature should decrease with the axial distance away from it. It is reasonable that the monomer's aromatic ring should break apart where the electric field is most intense, in the zone near the coil, while tending to remain intact further away. Likewise, the aniline should be more strongly oxidized near the coil. Placing substrates at various positions in the reactor appears to be a method of tailoring both the chemical structure of the polymer film and its associated electrical properties, but the latter aspect needs more detailed investigation.

Microscopic characterization

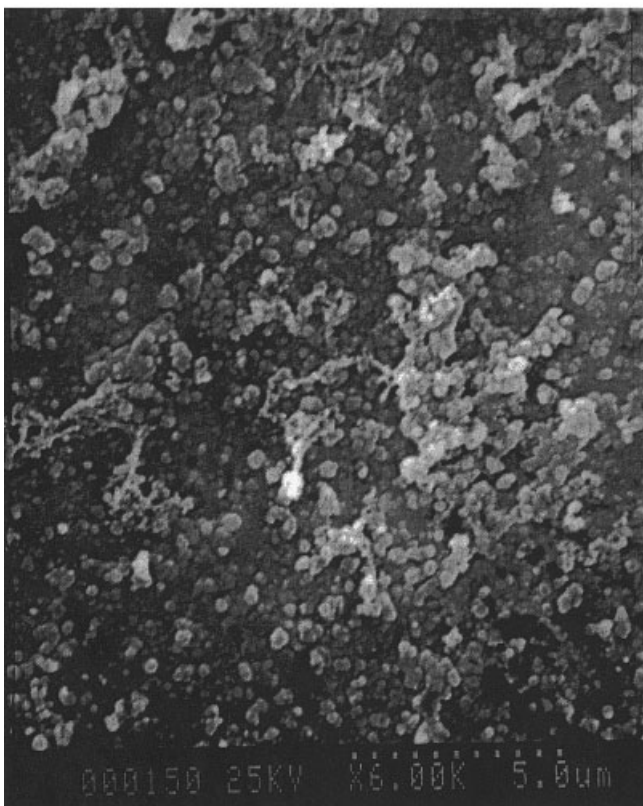
SEM images show that the substrate has a significant effect on the film morphology. A comparison of films grown under identical conditions on ITO glass, Si wafers, Al thin films on Si wafers, and Pt thin films on Si wafers indicates that smoother substrates result in smoother PAN films. Of the three conducting substrates, Al produced the smoothest deposits. Films deposited on ITO glass were the roughest and also adhered poorly. Silicon wafer substrates were used to determine whether the film morphology was also a function of thickness; the wafers themselves were extremely smooth but because of their poor conductivity they did not lend themselves to voltammetry or impedance spectroscopy and were not used in other phases of this study. PAN films deposited on Si with 50 plasma pulses were relatively smooth, whereas those made with 100 pulses were rougher and had nodules atop a smoother underlayer. [Fig. 2(a,b)]. The thicker films tended to have more pinholes; this effect was probably due to prolonged exposure to the plasma environment.

Internally, the microstructure of plasma-polymerized aniline is not homogeneous. TEM indicates roughly spherical inhomogeneities about 0.1 μm in diameter dispersed throughout the polymer [Fig. 3(a)], suggesting the presence of amorphous and ordered phases. Selected area electron diffraction (SAED) patterns of this material have faint rings with spots [Fig. 3(b)] and are consistent with short-range ordering of some type, possibly an oriented polymer network. Similar TEM observations have been reported for other plasma-polymerized materials,²⁷ and the dispersed spheres are considered to be a second phase embedded within the same polymer.

The nonuniformity of the PAN films is further supported by polarizing microscopy and by optical microscopy in the DIC mode. Birefringence was observed in plasma-polymerized aniline thin films but



(a)



(b)

Figure 2 SEM micrographs of PAN deposited on silicon wafers: (a) 40-Pa reactor pressure and 50 plasma pulses and (b) 40-Pa reactor pressure and 100 plasma pulses.

had several possible causes. These include the presence of two different phases, that is, regions with different optical properties; localized crystalline segments in the polymer; and elastic strain in the samples. Optical microscopy showed that the PAN surface was not uniform, but it could not probe the interior.

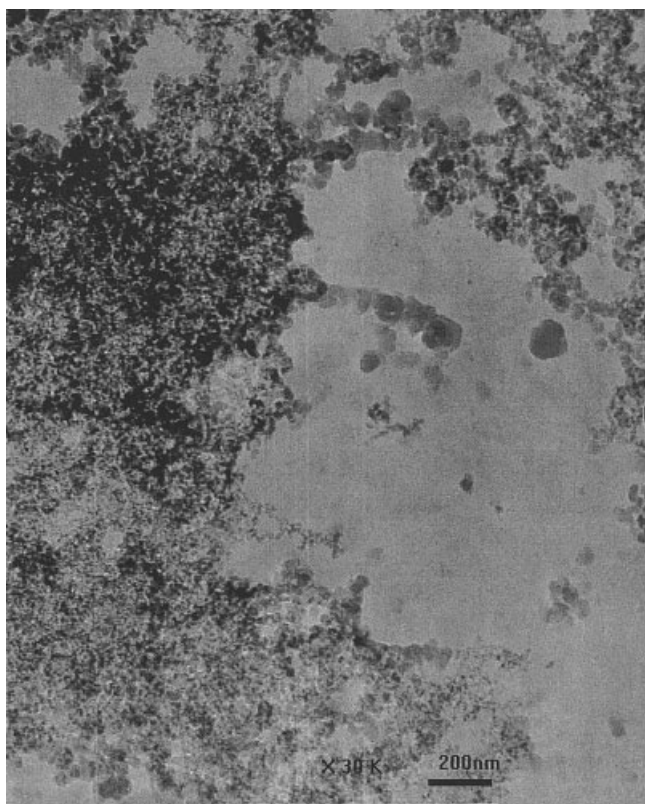
Voltammetry experiments

CV experiments allow direct comparisons of the electrochemical behavior of thin films of plasma-polymerized and electrochemically oxidized aniline. In addition, the electrochemical processes in plasma-polymerized aniline electrodes are interesting in their own right because PAN has a broad range of present and possible future applications in batteries and electronic devices. CV on plasma-polymerized thin films provides information on conducting paths and possible pinholes in samples, and it also provides support for results from other chemical characterization techniques.

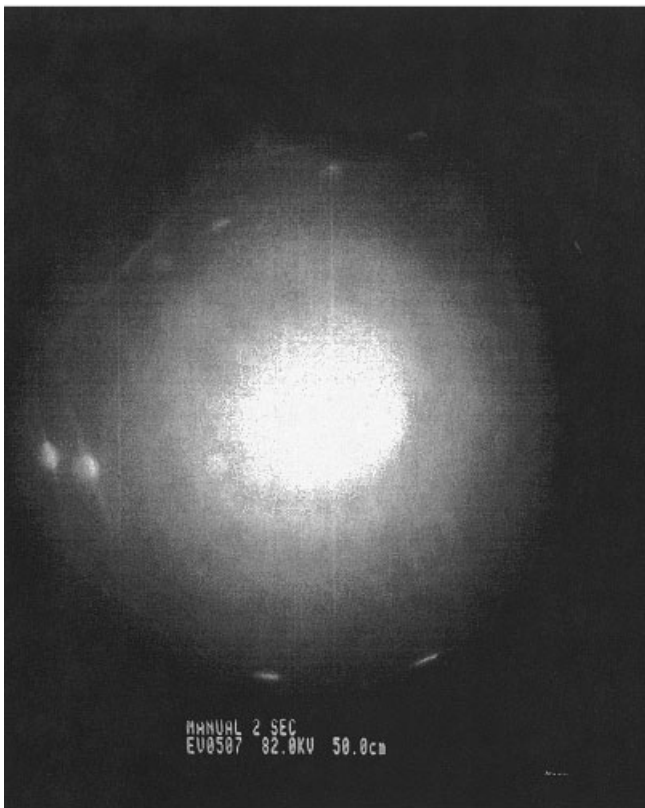
Significant differences were found in voltammograms obtained from plasma-polymerized PAN thin films grown on various conducting substrates. On platinum, the polymer layer showed essentially no electrochemical response, the behavior being characteristic of a blocking layer. In contrast, films grown on gold substrates had one anodic peak near 700 mV and one cathodic peak around 220 mV; this separation was consistent with kinetic irreversibility. A comparison of voltammograms for PAN/Au and uncoated Au electrodes strongly suggests that the cathodic peak on PAN/Au is in fact due to the Au substrate and that the polymer layer therefore must contain pinholes or pores. The anodic peak is probably attributable to the dissolution of the film. With repeated cycling in 1M HCl, there was a progressive decrease in the heights of both peaks. A visual examination of the electrode after voltammetry usually revealed several sites at which delamination of the PAN film and Au layer had occurred.

CV was also carried out for films deposited on ITO glass in 1M HCl and 1M H₂SO₄, with and without 0.2M aniline. By cycling PAN films in protonic acids with different anions, we could discern the effect of the anion on the position of the CV peaks. Previous work on chemically or electrochemically synthesized PAN has shown that there are differences in voltammograms obtained in different acids. In addition, the effect of the chemistry of the polymer film itself was explored with two series of samples grown at different locations in the plasma reactor: 31 cm, at which the FTIR spectra had prominent carbonyl bands, and 39 cm, with pronounced aromatic character. Results from the 31-cm series are discussed first.

In 1M H₂SO₄, three sets of peaks were observed during scans at 50 mV/s [see Fig. 4(a,b); the first potential sweep was anodic in the former case and

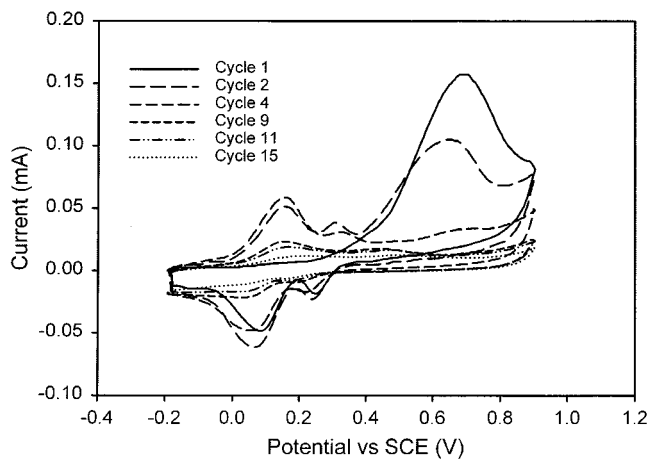


(a)

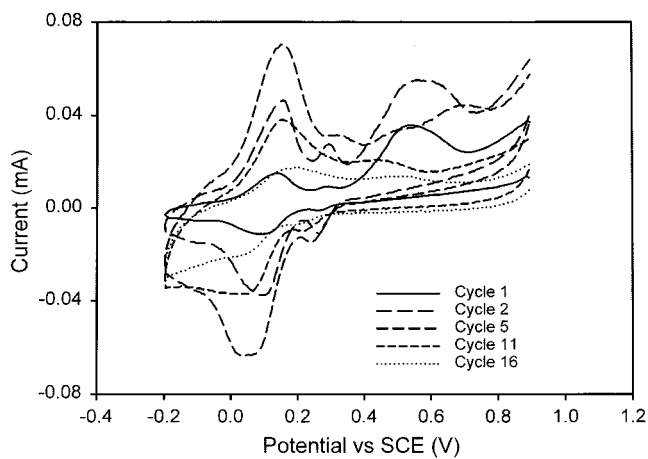


(b)

Figure 3 (a) TEM micrograph (80 kV) and (b) SAED pattern of PAN deposited on KBr pellets. The reactor pressure was 40 Pa, and there were 100 plasma pulses.



(a)



(b)

Figure 4 Cyclic voltammograms of plasma-polymerized aniline deposited on ITO 31 cm from the center of the RF coil (a) with the anodic sweep first and (b) with the cathodic sweep first. The sweep rate was 50 mV/s, and the H_2SO_4 concentration was 1M.

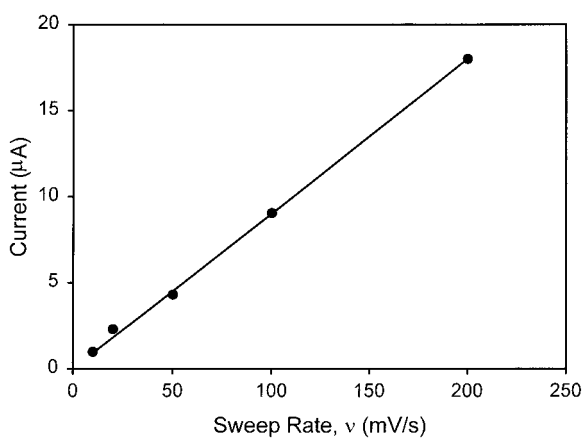
cathodic in the latter]. On the first cycle in Figure 4(a), there was an anodic peak near 700 mV (peak I) and a cathodic peak between 100 and 200 mV (peak II). Additional peaks grew in during subsequent scans, in the range of 250–400 mV (peak III). Figure 4(b) is very similar, except for the expected differences during the first cycle. Independent of the direction of the initial sweep, the magnitudes of all the current peaks increased for three or four cycles and then decreased as cycling continued. Once the electrochemical centers on the films were activated during the first one–two cycles, these cyclic voltammograms were quite similar to those reported for PAN films made by conventional chemical or electrochemical oxidation.^{13,20,21,23,28–33} One notable difference is that peak I did not have a cathodic counterpart, in contrast to the behavior of conventionally polymerized aniline. Interestingly, conventionally polymerized PAN, but not our plasma-polymerized samples, is an electrochromic material;

thus, the missing cathodic peak may be associated with electrochromic properties.

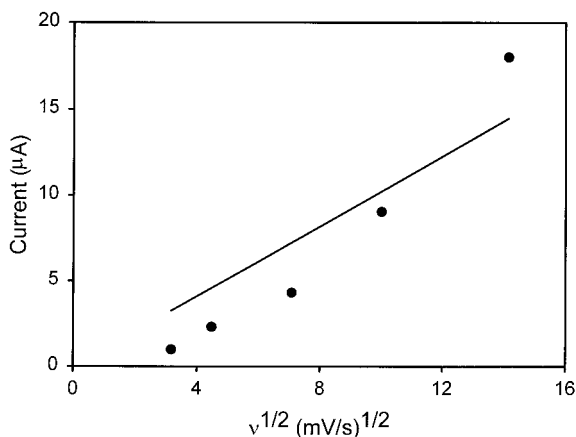
In conventional PAN, peaks II and III are diffusional and nernstian. A plot of the current peak height versus the square root of the potential sweep rate should be linear if the peak is due to a diffusional process; if adsorption is controlling, the peak height is proportional to the scan rate itself.³⁴ Figure 5(a,b) indicates that for the plasma-polymerized films produced in this study, peak III is associated with an adsorption process ($R^2 = 0.9993$), rather than diffusion ($R^2 = 0.9237$). For peak II, no conclusion is possible because graphs of the peak current versus the sweep rate and the peak current versus the square root of the sweep rate have virtually the same R^2 values (0.9525 and 0.9543, respectively).

In 1M HCl, plasma-polymerized PAN films had limited cyclability, and peak III was difficult to discern. Peak II was again due to diffusion.

A parallel series of experiments was performed with electrolytes that contained aniline as well as a mineral

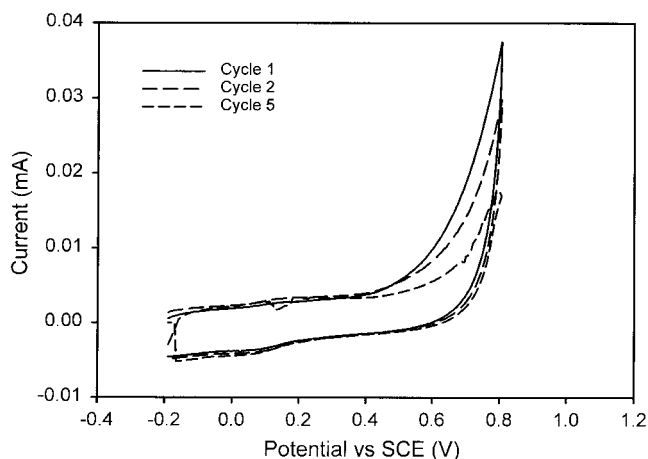


(a)

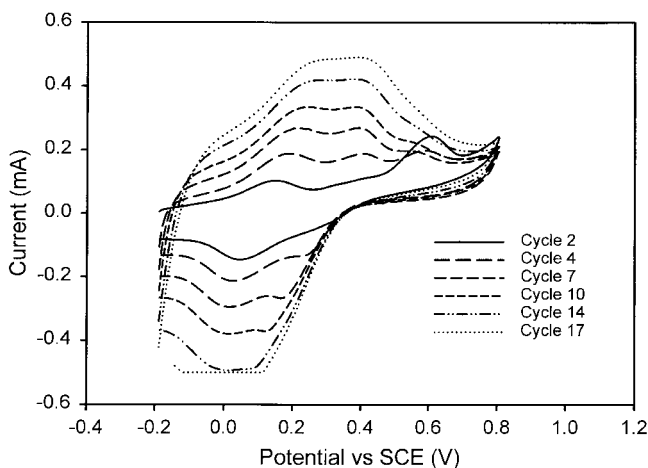


(b)

Figure 5 Effects of (a) the sweep rate (ν ; sweep rate = 50 mV/s; $[\text{H}_2\text{SO}_4] = 1\text{M}$; $R^2 = 0.9993$) and (b) the square root of the sweep rate [$\nu^{1/2}$; $R^2 = 0.9237$; see Fig. 3(a) for the conditions] on the peak III height.



(a)



(b)

Figure 6 Cyclic voltammograms of plasma-polymerized aniline deposited on ITO 39 cm from the center of the RF coil: (a) sweep rate = 50 mV/s and $[\text{HCl}] = 1\text{M}$ and (b) sweep rate = 50 mV/s, $[\text{HCl}] = 1\text{M}$, and $[\text{aniline}] = 0.2\text{M}$.

acid, namely, 1M $\text{H}_2\text{SO}_4/0.2\text{M}$ aniline and 1M HCl/0.2M aniline. In the presence of the monomer, the current peak heights increased with prolonged cycling. Visual examination showed that electropolymerization occurred at the edges of these electrodes, where the current density would be highest; in contrast to the yellowish-brown plasma-polymerized films, the electropolymerized deposits were electrochromic and green. The voltammograms resembled those recorded for aniline and its oxidation products.^{22,35} Mabbot's mechanism²² attributes peak I to a chemical reaction, peak II to reversible charge transfer, and peak III to adsorption; peaks II and III grow in with lengthy cycling as peak I diminishes. Yang and Bard²¹ gave a contrasting interpretation of peak III, regarding it as a result of the degradation of electroactive PAN.

Cyclic voltammograms of plasma-polymerized PAN/ITO films grown 39 cm from the RF coil of the

plasma reactor are shown in Figure 6(a,b). The electrolytes were 1M HCl and 1M HCl/0.2M aniline. Again, the current peaks decayed with time in the absence of aniline. The currents increased remarkably with continued cycling when monomer was available; a similar effect was seen in sulfuric acid media. Green deposits were again found after cycling in aniline-containing solutions but were more extensive in this series of samples, growing completely over the exposed working electrode. Thus, the greater aromatic character of PAn films deposited well away from the RF coil apparently made them more reactive toward aniline. Voltammograms in the 39-cm series were somewhat less complex than those for films grown at 31 cm, in that peak I was far less prominent. In addition, the 39-cm films rather quickly lost their distinguishing features upon repeated scans, whereas 31-cm films were better able to withstand extended cycling.

Impedance characterization

In previous work, plasma-polymerized aniline films were found to have low direct-current conductivity,²⁴ and so high impedance was expected for the three-layer sandwich cells. Significantly, pure capacitance behavior was not observed in any of the different cells tested. Very low impedance behavior was consistently seen in Au/PAn/Au and Al/PAn/Au cells and in some Al/PAn/Al sandwiches as well. These results are consistent with short circuiting between the top and bottom metal electrodes and are tentatively ascribed to the presence of pinholes in the middle polymer layer. The presence of pinholes is not unexpected because the PAn films are quite rough, and it is also suggested by SEM and CV results, as previously noted.

CONCLUSIONS

PAn thin films prepared in a pulsed-plasma reactor were characterized *ex situ* by complementary spectroscopic, electrochemical, microscopic, and impedance methods. The inductively coupled reactor operated at a higher RF power and higher energy per RF pulse than more conventional capacitatively coupled plasma reactors, and as expected, films grown on substrates placed where the electric field was strongest experienced greater disruption of the aromatic π bonds in the monomer. FTIR spectra indicated not only that the primary amine groups of the monomer reacted during film growth but also that trace oxygen was taken up by the films under the conditions of a high electric field. Samples grown 39 cm from the RF coil had a strong aromatic character that was missing in films grown closer, and they lacked the strong carbonyl bands associated with high-field conditions. Thus, the careful positioning of the substrates in the reactor provided a way of tailoring the film chemistry

and related properties. CV was used extensively in previous studies of electrochemically or chemically oxidized aniline, but this investigation appears to be the first to apply CV to characterize samples prepared in the dry, relatively low-vacuum environment of a plasma reactor. Voltammograms on plasma-polymerized aniline confirmed that its electrochemical behavior was very similar to that of the products of aniline oxidation in solution. SEM indicated that the growth morphology depended on both the substrate and the film thickness. Smooth and adherent thin films were readily grown on smooth substrates, but nodules were observed on rougher substrates such as ITO glass. Nodular morphology was more pronounced on thicker films, and there appeared to be a transition to nodular growth after the film reached a particular thickness. Both electrochemical and impedance results implied that pinholes may have been present in the films. Several types of microscopic evidence suggested that the films were largely amorphous but also contained dispersed regions that were more highly ordered. It is possible that the relative amounts of the ordered and amorphous materials could be tailored through changes in the reactor operating conditions, substrate location in the reactor, or choice of substrate.

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