Comparison of Chemically and Electrochemically Prepared Polyaniline Films. 1. Electrical Properties

Douglas Chinn, Joel DuBow, and Martin Liess

Department of Materials Science and Engineering, University of Utah,
Salt Lake City, Utah 84112

Mira Josowicz and Jiří Janata*

Environmental Molecular Sciences Laboratory, Pacific Northwest Laboratory,[†]
Richland, Washington 99352

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Thin films (<200 nm) of chemically prepared polyaniline cast from solutions of formic acid and electrochemically prepared polyaniline films grown on top of the chemical films are characterized electrochemically, by work function changes and by conductivity measurements. The oxidized and reduced films exhibit complex relaxation phenomena over time periods ranging from 1 to 900 h. Water is seen to play a key role in relaxation. An explanation of the relaxation phenomenon is suggested as being a change in the ratio of fully doped conducting material to nonconducting material based on a granular morphology. It is shown that the two polymers are nearly identical chemically and in their behavior with differences being mainly morphological.

Introduction

Polyaniline (PANi) has been subject to intense investigation because of its good conductivity, stability in air and interesting electrochemical behavior.[1] It has been proposed for applications in batteries, electrochromic displays, electromagnetic interference shielding and static dissipation, reprographics, cabling,[2] and for chemical sensors.[3] One of its drawbacks for technological applications is its poor processability, making it difficult to form into shapes or to deposit it on nonconducting substrates. PANi is unique among conducting polymers because of the presence of multiple oxidation states and different protonation states.[1] Polyaniline is a multicomponent system consisting of the polymer, water, and ionic dopants which must be present to satisfy the condition of charge neutrality. Without anions polyaniline is an insulator with resistance at least 6 orders of magnitude higher than that of the doped conducting state.

Polyaniline and other conducting polymers are known to “relax” after being driven to a nonequilibrium potential.[3–8] The relaxation is seen in solution as a slow change in the open circuit voltage of the polymer in an electrolyte solution or as a change in work function or resistance measured in a gas phase. Colors of PANi also change with relaxation. The relaxation phenomenon has been described[7] as being a structural chain reconfiguration following movement of counterions, a chain twist based on changing oxidation states, movement of ions to maintain electroneutrality, or a change in the polaron–bipolaron density (redox state).

The casting of thin films of polyaniline from formic acid has been described.[9] Those chemically obtained films are sufficiently conducting to be used as substrates for the subsequent growth of polyaniline films by electropolymerization.

Chemically prepared (PANiC) polyaniline films were spin cast on insulating substrates and electrochemical (PANiE) films were grown on top of the chemical films. Here we describe the characterization of two types of PANi by resistance/conductivity and work function change measurements. A comparison between PANiC and PANiE is made, and the relaxation behavior of the two materials is compared.

Experimental Section

The process for making PANiC has been described,[9] and the method for casting thin films have been described.[10] Aniline (Sigma) was polymerized in aqueous 1 M hydrochloric acid using ammonium peroxydisulfate (Aldrich 98% ACS reagent grade) as an oxidant. The resulting polymer was dried and then treated with NH_4OH to convert the as-made “PANiC HCl salt” to dedoped (nonprotonated) insulating “PANiC base”. This material is in the intermediate “emeraldine” oxidation state. It can be dissolved in 98% formic acid up to 3% by weight. For this work films were typically made from 2% solutions giving thicknesses near 200 nm. Formic acid (Sigma 98%) has a high enough vapor pressure so that it evaporates quickly when spin casting polyaniline/formic acid solutions. The thickness is

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* To whom the correspondence should be addressed.

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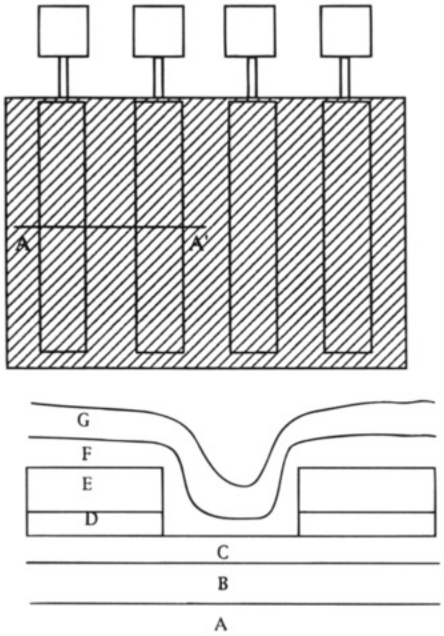

Figure 1. Diagram of substrate used to measure polyaniline thin film properties. Shown are a top view and a cross section through A−A′. Polymer is cross hatched area, four leads are platinum with an active area of 1.0 × 0.15 cm. Space between electrodes is 0.15 cm. (A) silicon substrate; (B) thermal oxide, 200 nm; (C) sputtered silicon nitride, 100 nm; (D) titanium/tungsten adhesion metal, 50 nm; (E) platinum, 200 nm; (F) PANiC, 80−250 nm; (E) PANiE, ~7.5 nm/cycle.

controlled by the concentration and the spin speed. The films made by this technique can be made in thicknesses up to 300nm with about ±15% uniformity. Formic acid was selected as the solvent in this work over organic solvents such as dimethyl sulfoxide (DMSO) and *N*-methylpyrrolidone (NMP) because of its high vapor pressure and ability to dissolve a large percentage of the polymer. Films cast from formic acid are in the conducting state (green), but the formic acid evaporates or can be washed out with acetone or water, leaving a poorly conducting film (blue).

The substrates used for all work are shown in Figure 1. Hexamethyldisilazane (HMDS) was used as an adhesion promoter. To define the active area, the polymer was masked off with positive photoresist and etched in an oxygen plasma, and the resist was then stripped off in acetone. The form of the substrate chip is shown in Figure 1. The platinum electrodes under the polymer are 0.15 cm × 1.0 cm and the bond pads are 0.15 × 0.15 cm. The spacing between the electrodes is 0.15 cm. The polymer area was 1.35 cm × 1.2 cm (1.62 cm^2). Resistance was measured by driving the current through the outside leads and measuring voltage drop on the inside leads by clamping the chip into a modified IC test clip (3M #923695-R). The test clip contacted the platinum bond pads and had copper lead wires soldered to it which were inserted into the interface board on a HP4145 semiconductor parameter analyzer.

Voltammograms were measured on a EG&G Model 273 potentiostat/galvanostat (PAR). To study the relaxation phenomena, the film potential was scanned in an acid electrolyte to the oxidation (+750 mV) or reduction potential (−100 mV) vs SCE. All potentials refer to SCE unless otherwise stated. The auxiliary electrode (15 cm^2) was platinum coated stainless steel. Typically three cycles were used on PANiC films to reach a steady state where the voltammogram retraced itself. After scanning, chips were soaked for 5 min in deionized water to rinse out any residual acid, blown dry, and then baked for 10 min at 60 °C to drive off any surface water. For some experiments the films were given a brief 2-s rinse and blown dry. The rinsing treatment of the films is a critical parameter because the value of the resistance depends on the treatment after doping or electrochemical work.

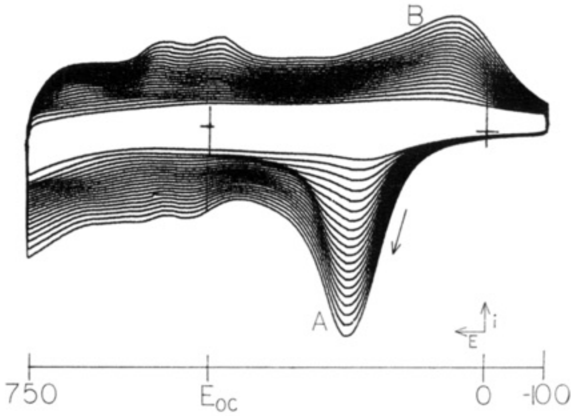

Figure 2. Voltammogram recorded during growth of electrochemical polyaniline on top of a chemical polyaniline film. Left cross is the open circuit voltage of the chemical film, right cross is the origin. Potential range is from +750 mV on the left to −100 mV (vs SCE) on the right. 10-s delays were used at the end of each half cycle. Current line represents 0.5 mA; the potential line 50 mV. The arrow represents the scan direction.

Electrochemical polyaniline (PANiE) films were grown on top of chemical films (PANiC) by cycling the potential in a 0.1 M aniline/1 M sulfuric acid solution. Potential was cycled between −100 and 750 mV with 10-s delays at the end of each cycle;[3,5] 30 mV s^{-1} scan rates were used unless otherwise specified. Typically 20 cycles were used and the current increased on each cycle indicating film growth (Figure 2). The voltammogram shows the development of two additional peaks at 450 and 650 mV after about 10 growth cycles. These peaks may be caused by non-para coupling of aniline radical cations.[11] Films grown beyond 20 cycles are powdery and exhibit poor adhesion to the substrate after 40 cycles. By driving the potential to higher anodic voltages (850 mV) thicker films could be obtained, but growth was primarily over the platinum electrodes and not in the areas between the electrodes. Film thickness was measured on a Dektak II profilometer. Optical characterization was done on a Nikon microscope.

For voltammetric measurements the polymer was scored along the platinum leads with a sharp knife in order to separate the PANiC deposited over the Pt leads from the PANiC deposited over the insulator. This was done to eliminate the *iR* drop in the portion of the polymer not in close contact with the platinum leads. Without this separation a peak broadened by the *iR* drop in the film was obtained.

The work function (WF) change was monitored with a Kelvin probe (KP) (Besocke Model 07,[12,13] Figure 3). It was modified to accept large chips with four lead wires for simultaneous resistance and WF measurements. The vibrating capacitor was mounted in an aluminum block. The substrates with the polyaniline films were mounted on a base which could be adjusted vertically to control the distance between the vibrating electrode and the substrate. Four gold-plated pins which contacted the four square pads on the chips were also mounted on the base. The pins were higher than the block, protruding into the lid. A polyurethane pad was inserted into a cavity in the lid and when the substrate was brought near the vibrating electrode. It exerted pressure on the gold pins, ensuring a good contact to the leads. Each lead was contacted separately. For work function change measurements all four leads were shorted together. They were monitored independently for resistance measurements. Resistance measurements made inside the KP chamber agreed well with those made externally. Relaxation work function change measurements were made in laboratory air. Humidity-dependent work function measurements were made in dry

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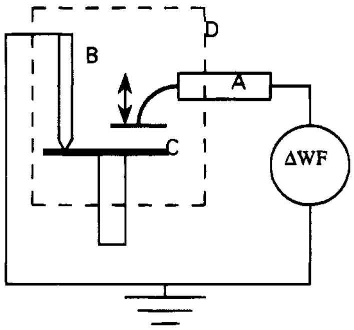

Figure 3. Kelvin probe configuration used to measure work function change and resistance change on the same sample. The work function measurement had to be interrupted to measure four-lead resistance. For work function four leads were shorted together to ground but were separated for resistance measurement. Current was driven in the outer contacts and the voltage drop was measured across the inner contacts. Resistance was taken as the slope of the $i-V$ curve through the origin. (A) vibrating capacitor; (B) pin used to contact the four bond pads; (C) silicon chip with metal pattern and polyaniline film; (D) dotted line represents the chamber enclosing the chip.

nitrogen or in nitrogen bubbled through water to achieve 100% relative humidity. The vibrating probe was over both the metal and polymer parts of the substrate.

Results and Discussion

Voltammetry. As prepared (nondoped) PANiC films were doped in four different acids: sulfuric acid, trifluoroacetic acid, perchloric acid, and hydrochloric acid. During this immersion doping the open-cell potential, E_{oc}, stabilized near ~500 mV. The films were then cycled yielding cyclic voltammograms that were similar in peak placement and shape. According to Huang et al.,[1] two protons and two electrons are given off, followed by two more protons and electrons, a total of four for the first peak (peak A in Figure 2). Others have suggested the incorporation of cations concurrent with the expulsion of the anions as the means of maintaining the electroneutrality of the bulk of the polymer.[14,15]

Conductivity measurements for films doped in the four acids are also similar. The conductivity of conducting polymers depends primarily on the anion used in the synthesis and does not vary when a different anion is exchanged into the matrix because the molecular structure is defined in synthesis. This applies to both PANiC and PANiE. Growing PANiE films on top of PANiC films results in the curve shown in Figure 2.

Polymers are expected to swell upon doping and hydration. Quartz crystal microbalance measurements[14-16] indicate large mass increases through the first peak, even though protons are lost, the mass gain coming from anions which are incorporated into the film. Even though the polymer is hydrophobic it is known to absorb water.[17] Given the mass increase, the volume change would be expected to be large. However, our data indicate no significant thickness changes in PANiC upon immersion doping or upon soaking in water. This suggests that the density of films increases upon doping. Films described below were doped prior to voltammetry.

Typical E_{oc} of immersion doped PANiC is around 500 mV (with a measured range of 430-650 mV) in 1 M sulfuric acid. In a similar experiment, E_{oc} of an undoped PANiC base film in deionized water is approximately 240 mV. There is no major significance in this value as the exchange current density of the ion exchange into the undoped film is low and therefore the E_{oc} is poorly defined.

Microscopic examination of PANiC films reveals a smooth featureless film. PANiE films show a rougher surface, with obvious nucleation sites of small areas of PANiE. As the film gets thicker, these features become more prominent, eventually transforming into a powder that does not adhere to the underlying layers.

Diffusion of Ions in the Film. To estimate the diffusion coefficient of anions in the PANiC film, sweeps were done at various scan rates (10-170 mV s^{-1}), and the current measured at the 200 mV peak. Equation for semiinfinite diffusion in solution was used:[18]

$$i_p = (2.69 \times 10^5) n^{3/2} A D_0^{1/2} v^{1/2} C_0^*$$

where i_p is peak current, n is the charge on the permeating ion (-1 in all cases), A is the geometrical area of the film, D_0 is the effective diffusion coefficient ($cm^2\ s^{-1}$) in the film, v is the scan rate, and C_0^* is the bulk concentration of the anion in the solution. It is assumed that the bulk concentration of the anion in the solution is approximately the same as the concentration of the same anion in the polymer. This assumption may not be justified, and therefore the estimates are only approximate. This equation yields diffusion coefficients of $4 \times 10^{-10}\ cm^2\ s^{-1}$ for 1 M ClO_4^-. The diffusion coefficient for HSO_4^- is 4×10^{-10} for 1 M and $6 \times 10^{-9}\ cm^2\ s^{-1}$ for 0.1 M sulfuric acid, in good agreement with the other acids and in agreement with other work[19] where sulfuric acid is reported to behave as a monovalent anion in polyaniline. The diffusion coefficient of water in polyaniline has been reported as $4 \times 10^{-10}\ cm^2\ s^{-1}$.[20]

The diffusion coefficient was also determined in acetonitrile (ACN) using CF_3COOH as an acid and $LiClO_4$ as an electrolyte in order to increase conductivity.[21-25] A Ag/0.01 M $AgNO_3$ in ACN//0.01 M TBATFB in ACN was used as a reference electrode, scanning between -400 and +500 mV. This technique yielded the H^+ expulsion peak at +200 mV at 10 mV s^{-1}, shifting to 350 mV at 170 mV s^{-1}. The H^+ comes back on at +50 mV at 10 mV s^{-1} and -50 mV at 170 mV s^{-1}. The calculated diffusion coefficient is $1.3 \times 10^{-9}\ cm^2\ s^{-1}$.

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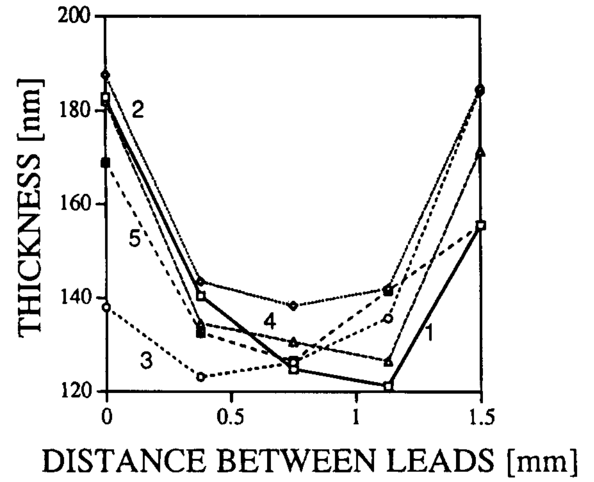

Figure 4. Thickness vs position for electrochemical films grown on chemical films. Center to edge variation is due to inherent resistance in the chemical films during the growth. Films were grown for 20 cycles between −100 and +750 mV vs SCE. Measurements were taken between leads (see Figure 1). Acid and scan rate use for each curve: (1, □) HCl 40 mV s^{-1}; (2, ◇) HCl 30 mV s^{-1}; (3, ○) HCl 20 mV s^{-1}; (4, △) H_2SO_4 50 mV s^{-1}; (5, +) H_2SO_4 30 mV s^{-1}.

Resistance Measurements. Because of the resistivity of the film and the corresponding *iR* voltage drop, the polymer above the platinum leads is exposed to a higher potential than the polymer which is above the space between the leads. Figure 4 is a plot of thickness vs position for a 20-cycle PANiE film between two platinum leads at various scan rates. The fact that resistance is distributed across the film is further confirmed when a PANiC film was spun on a glass substrate and oxidized or reduced. A color gradient could be seen in the window between platinum leads with the color corresponding to the most oxidized or reduced state being nearest the platinum. A gradient of color can also be seen on PANiE films grown on PANiC films.

After immersion doping, the conductivity of a "wet" PANiC film after a brief rinse and blow dry was 0.2 S cm^{-1}. The conductivity decreased to 0.04 S cm^{-1} after a 5 min rinse and a blow dry and decreased again to 0.03 S cm^{-1} as a "dry" film after baking. Both wet and dry films change unpredictably in conductivity with time in air by about 15%, probably due to humidity changes. In agreement with the work of Neoh et al.,[19] protonation/doping depends on the time of rinsing. This may account for the variations in conductivity. The exact redox/doping state of the polymer based on time, water, and acid content and room humidity is not well defined. Wet and dry films give similar results for many experiments, but the dry films show more consistent behavior. Films given no rinse and only a blow dry had sulfuric acid droplets on the surface.

Relaxation in Polyaniline. Polyaniline is a multicomponent material, consisting of polyaniline chains of various lengths and configurations in space, dopant anions, and protons, and water. Conduction in polyaniline has been described using the two "phase" or two "region" granular morphology mixture model originally proposed by Ginder, et al.[26] This model which is supported by a number of diverse experiments[27−34] postulates a conducting region in the ideal emeraldine oxidation state (the conducting or metallic region) when all imine nitrogens are protonated. There is one proton/anion for every two monomer units and probably a specific number of water molecules associated with each anion. The conducting regions are surrounded by a matrix of "nonconducting" or "insulating" polymer regions in an as-yet-undefined oxidation/doping state. Electron transfer between these regions is controlled by charging energy limited tunneling (CELT).[27] Domain sizes on the order of 20−30 nm,[33] to as small as a single chain[30] have been reported. If the volume of a conducting phase is as low as 5 nm^3 [34] to 27 000 nm^3 (the volume of a 30 nm domain 30^3), this volume is too small to be a single chain, given that the molecular weight of PANiC is reported on the order of 64 000,[35] or over 600 repeat units. The polyaniline chain is stiff because of its conjugated structure and is not likely to exhibit long range order or to fold back on itself to crystallize. A benzene ring is estimated to be ~0.5 nm in length, so a conducting "domain" on a chain would consist of as little as four repeat units, the minimum allowed to define the emeraldine state. A conducting domain has a higher level of order than its surroundings.

The role of water must be understood as it effects both work function and resistance. Water is known to exist in two states in polyaniline[20] as "water of hydration" which is tied as one water molecule to each aniline repeat unit and as a "free water". Figure 5 is a plot of work function and resistance of a rinsed and baked PANiC film under dry nitrogen as water is introduced as 100% relative humidity (RH). A minimal amount of water is needed for the polymer to be at equilibrium with the air because the first time a well dried film was exposed to wet nitrogen the work function and the resistance both decreased. Then when a film is allowed to come to equilibrium in a dry nitrogen stream, the introduction of 100% RH causes a very rapid increase of 100 mV in work function and an almost as rapid decrease in resistance. Turning the humidity off results in a rapid recovery of the work function but a slow increase in the resistance. This is in agreement with ref 29, where water diffuses in fast and diffuses out slowly. The rapid change in WF is indicative that the surface component of WF is affected by water, but the resistance response is mostly dominated by the bulk behavior. Bulk resistance behavior dominates surface resistance behavior.

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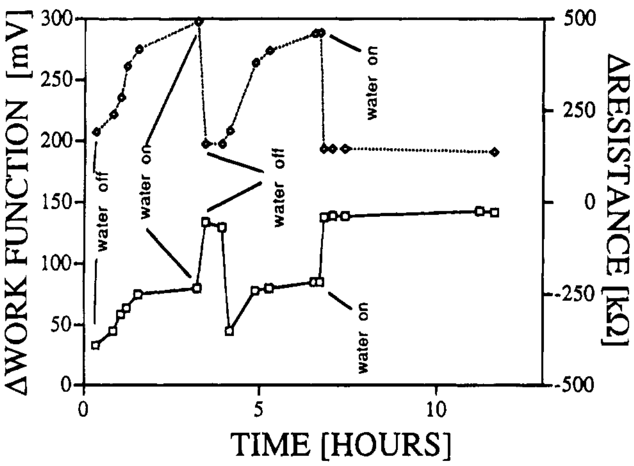

Figure 5. Response of PANiC to water vapor. Dry nitrogen was used as the carrier gas. After coming to a steady state in dry N_2, the film responds to 100% humidity by decreasing resistance and increasing work function. The WF change is immediate, indicating a surface phenomenon, but resistance changes slowly, indicating a bulk response.

The voltammogram shows little change when scanning after allowing relaxation, except for slightly decreased currents, indicating decreased capacitance. Scanning the potential in sulfuric acid after relaxation in air for one week failed to change the shape of the voltammogram. Holding a film at 700 mV vs SCE in 1 M H_2SO_4 over night flattened out the peaks and reduced the current. Holding a film at −100 mV for an hour failed to make significant changes in the voltammogram.

Relaxation also takes place in air where the external circuit is open, indicating that the usual redox reactions are not happening and carriers cannot move in and out of the closed system. Water can evaporate, but the acid cannot. However, concentration of water in the polymer determines the protonation ability (acidity) of the remaining acid.[36] For the material to change oxidation states *in air*, there must be a source/sink for electrons as the oxidation state/doping level changes. This function may be served either by the metal substrate, by internal redox rearrangement (disproportionation) within the polymer itself or by atmospheric oxygen. The first two changes would lead to a change of the contact potential between the polymer and the metal, while the third would result in a chemical change of the polymer.

Figure 6a represents relaxation behavior of a PANiC film in air oxidized to 750 mV, and Figure 6b represents a PANiE film. From the oxidized state the work function and the resistance both decrease with time. Resistance is highest immediately after removing the film from solution, in agreement with solution resistance measurements. (Open-circuit potential measurements after relaxation show that E_{oc} is near 450mV). It takes about 1 h for WF and R to come to equilibrium before any trends in change can be observed. Resistance for PANiE shows an order of magnitude decrease in 1000 h, and PANiC decreases by a factor of 3 in 400 h. For PANiC films the first value of resistance measured after oxidation was about 3 times higher than that of the starting PANiC. Resistance decreases linearly with the square root of time for about 25 h. At longer times the resistance approaches its limiting value. Films have been monitored for over 900 h.[10]

Figure 6c represents the relaxation in air of a PANiC film reduced to −100 mV and Figure 6d represents a PANiE film. From the reduced state, work function also decreases by 300−400 mV, but resistance increases as the polymer relaxes by a factor of 3 or less, a trend opposite that in solution. For PANiC films the relaxation started with a resistance very near that of the film before reduction treatment. Resistance increases linearly with the square root of time.

The potential applied to oxidize the film pulls dopant anions (and/or expells cations) into the film, making it more p-type and driving the Fermi level (E_f) down, closer to the valence band. The oxidized state represents a p-type material and the Fermi level should be going up inside the bandgap as the polymer relaxes. The work function change seen can be accounted for with the polymer changing from primarily one-phase to a two-phase material whose average work function is smaller than that of the oxidized phase. The oxidized state is highly doped and the fraction of the nonconducting (bipolaron) regions is high. As the film relaxes the ratio of polaron/bipolaron increases and the conductivity decreases.

On the other hand the applied negative polarization drives anions out of the film, giving the polymer a less p-type state. As the polymer relaxes, the Fermi energy raises again in the bandgap, thus decreasing the work function. Conventional theory says that resistance should decrease as the reduced material relaxes toward the emeraldine state due to the increased number of polaron states. This is not however observed.

The change of mobility is a plausible explanation of the increased resistance; Relaxation is interpreted as an internal rearrangement between regions, driven by a gradient in chemical potential of water and acid between the two regions. The conducting region has high order with specific proton/anion and water contents. The ordering of the polymer may be accompanied by a twisting of the chain. The nonconducting region is the source and sink for water and protons and its composition varies with time. E_{oc} in solution or the relaxed polymer in air is a minimum free energy state where the polymer has phase segregated into these two regions whose volume ratio determines the resistance and work function of the polymer. Conductivity σ is given by the product of n, the carrier density, e, the carrier charge, and u, the mobility: $\sigma = neu$. With a high doping density mobility should be low. The system conductivity must be dependent on the second phase which is not in an optimum conducting state. With excess dopant the barrier between the two regions is high. PANiC is approximately 42% in the protonated emeraldine salt state as it is made[10] based on the ratio between the dopant and nitrogen, but no water was detected in these samples. Doping with HCl increased the protonation level to 50%. If the conducting phase is 50% protonated, the insulating phase must be proton deficient or have excess anion in it.

Role of Water in Relaxation. A series of experiments were performed in which the rinsing out of the acid was done very quickly (~2 s) followed by blow-drying of the film. It was thought that this rinsing time

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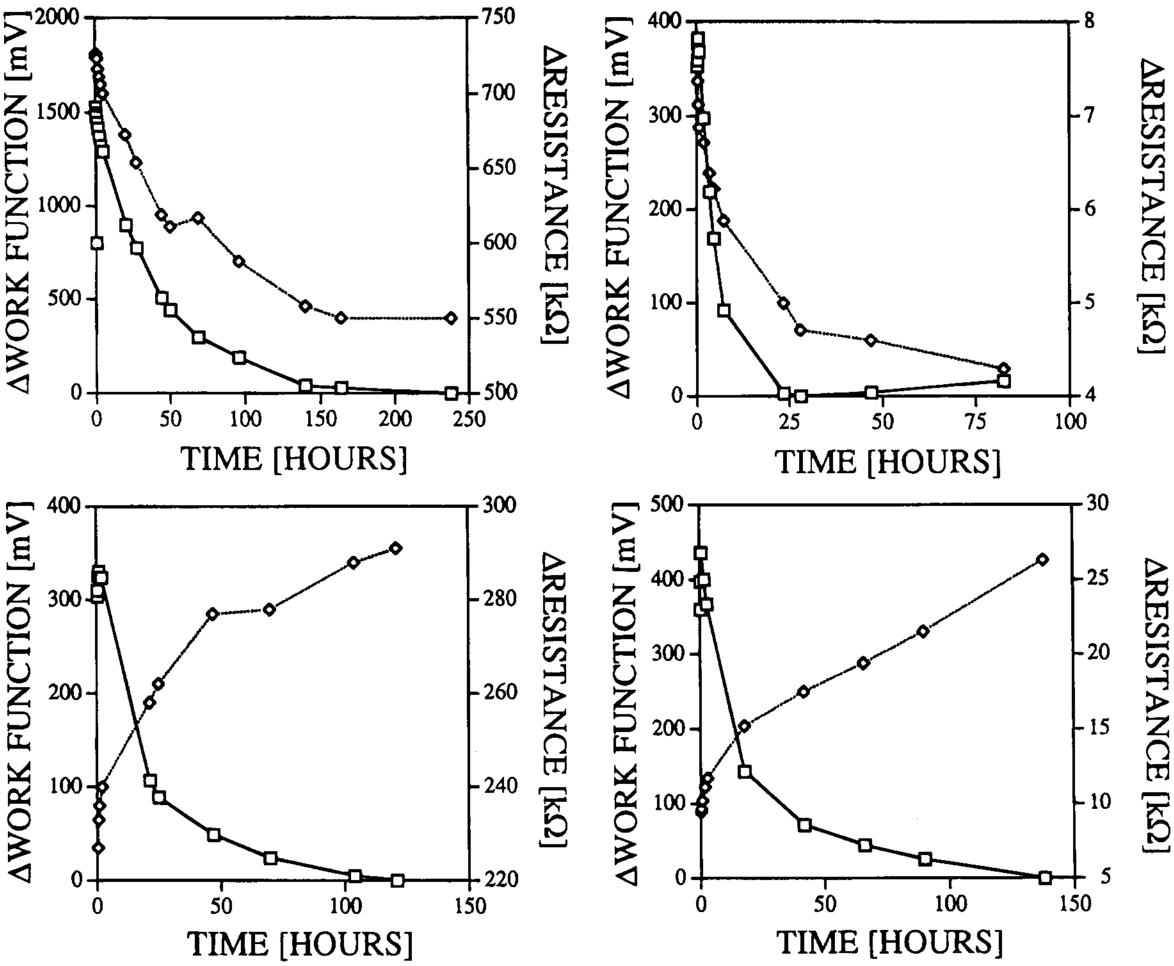

Figure 6. Work function change and resistance change vs time. (a) PANiC film relaxed from +750 mV in air. Work function and resistance both decrease for oxidized films after 1 h of coming to equilibrium with the air. (b) PANiE film relaxed from +750 mV in air. (c) PANiC film relaxed from −100 mV in air. Work function decreases and resistance increases for reduced films. (d) PANiE film relaxed from −100 mV in air.

would be sufficient to remove all excess sulfuric acid. However, even a visual observation confirmed that this is not the case because droplets of residual acid could be seen on the surface. The contribution of the residual acid to the overall conduction process must be small. This was confirmed by driving wet films to high potentials where ionic conduction would have shown up as a change in conductivity. However, residual acid may protonate the −NH− bridges depending on the concentration of free uncoordinated water in the film. Indeed, films with a high content of residual acid exhibited marked changes of conductivity when they were exposed to atmosphere of different relative humidity. We interpret this behavior to be due to the altered protonation ability of the sulfuric acid in essentially hydrophobic interior of the polyaniline film.[36]

Conclusions

The focus of this paper was on comparison of electrical properties and behavior of *chemically* and *electrochemically* prepared thin films of polyaniline. Globally, it is possible to conclude that the two types of polyaniline as assessed by work function and the conductivity are identical. Changes of work function and resistance due to relaxation are similar for both chemically and electrochemically made films. Decrease of work function and resistance seen in both polymers during relaxation from positively polarized state are consistent with the upward movement of the Fermi level. Following the negative polarization work function again decreases but there is a small increase of the resistance due to the decreasing mobility of the carriers. Relaxation is consistent with the model of movement of water and dopants between fully conducting regions and the surrounding insulating regions. The identical behavior of these two materials is particularly important for applications in which electrochemically grown polyaniline needs to be deposited over insulating substrates.

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