XPS Evidence of Redox Chemistry between Cold Rolled Steel and Polyaniline

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The electrochemical response of polyaniline (PANI) in its undoped intermediate (emeraldine base, EB) oxidation state coated on cold rolled steel (CRS) or glass substrate has been evaluated by X-ray photoelectron spectroscopy (XPS). The oxidation state of the polymer was determined from the ratio of amine vs imine nitrogen chemical states observed in the N(1s) photoelectron spectrum. A room-temperature air-dried PANI coating cast from NMP solution onto CRS was found to be reduced relative to its as-synthesized, air-stable state. Heating the PANI coated on CRS in the absence of air (165 °C, in ultrahigh vacuum) produced an even deeper reduction, resulting from the transfer of electronic charge to the polymer from the metal substrate. Subsequent brief exposure of this reduced PANI coating to air at elevated temperature (165 °C) reoxidized the PANI to the EB state. Analogous treatment of a PANI coating on glass caused no such change in the oxidation state of the polymer. Unlike steel, which provides a redox couple with PANI, glass is electroinactive. These findings are consistent with the hypothesis that PANI-EB can catalyze or otherwise enable passivation of steel surfaces, through electrochemical interaction with steel substrate. Neat PANI-EB heated to 200 °C under N_2 within an FTIR diffuse reflectance cell demonstrated loss of interchain H-bonding, presumably leading to softening. The FTIR spectrum of PANI-EB which had been exposed to air at 200 °C gave no indication of polymer oxidation.

Introduction

The greater part of the vast recent literature on polyaniline has concerned the electrical conductivity of protonic acid "doped" materials. The redox properties of the undoped polymer, however, may ultimately have greater economic importance. Polyaniline stands out among conductive or conjugated organic polymers for its relative ease of handling and fundamental low cost. A literature report of a blue solid deposited onto platinum metal in the electrochemical oxidation of aniline indicates that the polymer was prepared as a coating on metal, though unrecognized as such, in a laboratory 134 years ago.[1] In the past 15 years specific observation of the anticorrosion action of polyaniline has come from Mengoli et al.,[2] DeBerry,[3] and Ahmad and MacDiarmid.[4] The use of conducting polymer coatings, including polyaniline, for protecting mild steel from corrosion was discussed by Troch-Nagels et al.[5] Recent reports from Wessling and co-workers[6] and from Epstein and Jasty[7] give support to the claim that polyaniline effects a passivation of steel or iron.

This work investigates the origin of the protection which polyaniline affords steel. A polymeric coating capable of electronic interaction with substrate steel could enhance the metal's capacity to form a protective oxide. Interfacial charge transfer examined in this work is comparable to that observed by Salaneck[8] in the aluminum metallization of poly(3-octylthiophene), where metal near the polymer surface is seen to be electron deficient.

The work reported here derives from consideration of the reported cyclic voltammetry of undoped polyaniline:[9] the polymer in the intermediate emeraldine base (EB) oxidation state appears to be capable of oxidizing iron. However because air can reoxidize the leucoemeraldine base form of polyaniline (LEB) to EB, changes in polyaniline in contact with iron are likely to be seen only in the absence of oxygen. We made the further assumption that if metal−polymer redox chemistry were possible, it would be more facile under conditions of more intimate electrical contact. Our measurement of the thermal behavior of neat PANI-EB[10] suggested that we heat the coated metal sample to between 150 and 200 °C.

This report gives evidence of reduction of polyaniline by steel and suggests that steel so oxidized is rendered capable of forming a protective oxide, as has been independently proposed on the basis of other evidence by Wessling.[6] New data that indicate reduction−oxidation chemistry between PANI-EB and steel include the following: N(1s) XPS of a neat PANI-EB pellet;

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N(1s) XPS of NMP solution cast PANI-EB film on steel or glass at room temperature and 165 °C; N(1s) XPS of PANI film on steel after heating to 165 °C in the spectrometer vacuum chamber. The N(1s) XPS data of PANI coated on steel indicate reduction of PANI-EB to PANI-LEB. The observation that the PANI-LEB coating is oxidized in air to PANI-EB suggests a regenerative protecting capability of the polymer.

FTIR data are added to demonstrate the absence of bulk oxidation of PANI by exposure to air at 165 °C or higher. These data also show that there are modest structural changes in the PANI which could enable better electrical and mechanical contact of PANI with a surface at elevated temperature.

Experimental Section

Polyaniline emeraldine base was prepared in the oxidative polymerization of aniline with ammonium persulfate according to the method of MacDiarmid et al.[11] Coupons of unpolished, unpretreated cold rolled steel (CRS, ACT Laboratories Inc., Hillsdale, MI 49242) were cut into roughly 1 cm^2 samples and were cleaned of shop oil by immersion in and wiping with acetone and 2-butanone. The small coupons were immersed in or flow-coated with a 5% solution of PANI-EB in NMP (w/w) and were dried under ambient conditions for several days before being placed in the XPS vacuum chamber. A similar procedure was performed for the preparation of a thin PANI-EB film on glass microscope slides. Duplicate films, whether on CRS or glass were dried at 165 °C in air for 1 h. The thickness of these films was ca. 10 μm. Pressed pellets of neat PANI-EB were prepared (7 mm diameter, ~0.5 mm thickness) in a handpress. Examining pellets prepared from neat polymer, we could study the XPS of PANI-EB without interference of NMP solvent.

An air-dried solution cast sample was heated to 165 °C within the vacuum chamber of the XPS spectrometer where spectra were collected at various stages of heating. After data collection at 165 °C, the sample was cooled, removed from the vacuum chamber, then heated to 165 °C for 8 min in the laboratory atmosphere. Heating in the laboratory was performed on a DATAPLATE digital hotplate/stirrer. The sample was then returned to the sample chamber for XPS measurement.

Photoelectron spectra were collected with a Physical Electronics 5600 electron spectrometer employing either Mg or monochromatic Al Kα excitation. Base pressure in the analysis chamber of this instrument is 1×10^{-10} Torr. Upon heating PANI coated samples, the pressure rose to $\sim 1 \times 10^{-9}$ Torr, indicating negligible outgassing. Survey (broad energy range, low resolution) spectra were collected to determine the elemental composition of the sample surface. High-resolution spectra of the N(1s) and C(1s) core levels were collected to determine the chemical/bonding states present in the PANI. XPS is a highly surface sensitive technique, providing information on the outermost 5 nm of the sample. In this work we postulate that the chemical states observed at the outer extreme of the coating are representative of the bulk coating.

FTIR spectra were collected with a Nicolet 20 SXB spectrophotometer operated at 4 cm^{-1} resolution. Diffuse reflectance spectra of the polyaniline powder were collected with the Spectra Tech Collector attachment fitted with the catalyst reaction heater. Heating of the sample was performed within the flowing purge (N_2) of the sample compartment, with the cover dome of the catalyst chamber removed. Temperatures were raised by 20 °C increments to a final temperature of 200 °C. Each temperature was held for ~30 min before progressing to higher temperature. High-temperature oxidation of PANI was assessed at 200 °C by opening the sample compartment for 30 min to the laboratory air.

Adhesion of the PANI coating was tested by the tape method: a single edged razor blade was used to cut lines through the coatings into the substrate steel. Sets of perpendicular lines were scribed about 1 mm apart to create 1 mm^2 “boxes” of over an area of about 1 cm^2 in the coating. Scotch brand Magic tape was then applied with thumbnail pressure over the entire scribed area and was subsequently removed by slow peeling with pulling back of the tape in a direction parallel to the plane of the coating. The approximate areas of the metal made bare by this process are reported.

Results

XPS Results. Polyaniline comprises groups of phenylenediamine and quinonediimine units, and the oxidation states of polyaniline differ by the relative amounts of these units, from the fully reduced leucoemeraldine polyphenyleneamine to the fully oxidized polyphenyleneimine.[12] The air-stable intermediate oxidation state emeraldine form has *approximately* equal amounts of imine and amine nitrogen. Kang et al. have demonstrated[13] that the N(1s) XPS spectrum of PANI-EB can be fitted with peak components at 398.2 ± 0.1 eV, C=N (imine); 399.4 ± 0.1 eV, C−N (amine); and a low intensity component at ~401 eV. The ~401 eV peak is poorly defined, having been attributed to protonated amine groups, surface oxidized nitrogen, or cyclic structures as proposed by Demaret et al.[14] The N(1s) spectrum of the leucoemeraldine base (fully reduced PANI state) shows a single nitrogen environment at about 399.3 eV.[13]

XPS N(1s) data (Figure 1a) for a pressed pellet of PANI-EB is fit to two components in excellent agreement with Kang et al.,[13] Demaret et al.,[14] and Dillingham et al.[15] The amine chemical state accounted for 65% of the nitrogen, while the imine made up the remaining 35%. The pellet does not show any higher binding energy components, that often appear in solution cast samples. Note that although the EB state is often described as “50% oxidized”,[13] XPS data here and in the cited papers indicate more amine than imine in the air-stable polyaniline.

Carbon(1s) data (Figure 1b) from the PANI-EB pressed pellet also demonstrate the relative amounts of C−N

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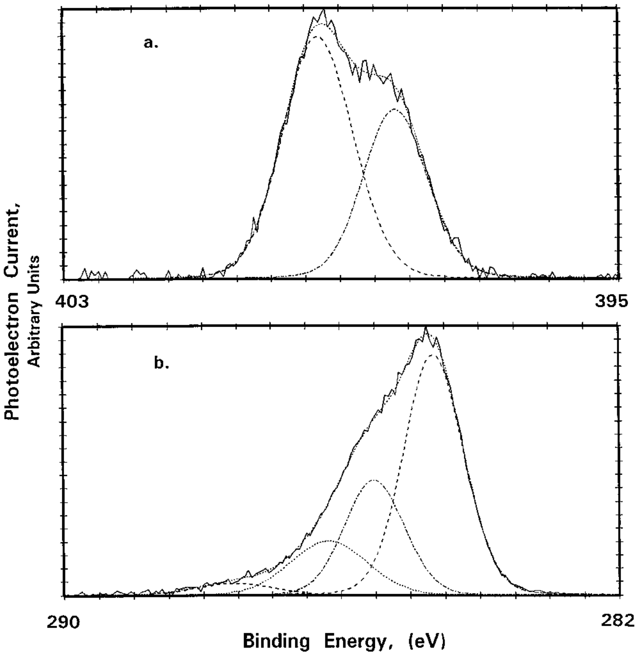

Figure 1. XPS spectra from PANI-EB solid pellet: (a) N(1s) spectrum showing amine (399.4 eV) and imine (398.2 eV) chemical states. (b) C(1s) spectrum showing 285.5 eV peak from C−N (amine) bonding and 286.2 eV peak from C═N (imine) bonding. Dotted lines showing fitting to Gaussian/Lorentzian line shapes.

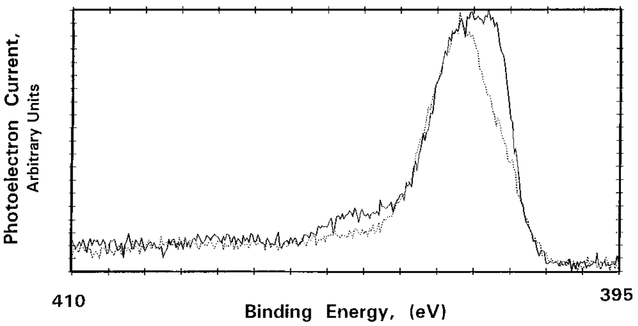

Figure 2. N(1s) spectra from PANI-EB coated CRS: (a) room-temperature dried (dotted line); (b) 165 °C dried (solid).

and C═N by the peaks characteristic for these bonding environments. Carbon singly bonded to N was observed at 285.5 eV, C═N was observed at 286.2 eV, and the C−C peak appears at 284.7 eV. The ratio of C−N to C═N peak area was in very good agreement with the N(1s) results.

Figure 2 shows the N(1s) spectra of PANI-EB coated on CRS from NMP solution. The spectrum from room-temperature dried PANI-EB on steel (Figure 2a, dotted line) is dominated by the amine component appearing at 399.4 eV. Imine nitrogen is evident only as a shoulder on the low binding energy side of the amine peak. The relative amount of amine present in the room-temperature air-dried PANI coating on CRS increased to an amine/imine ratio of 4.0 from a ratio of 1.8 (PANI-EB pellet). The change in the chemical state of the PANI indicates to the reduction of the PANI in contact with CRS. A duplicate sample air-dried at 165 °C yielded the N(1s) spectrum in Figure 2b, solid line. At elevated temperature the oxidation of PANI by air is enhanced as indicated by the increased imine concentration. The amine/imine peak area ratio for this sample was 1.5. Additional nitrogen chemical states appeared at 401.0 and 402.6 eV.

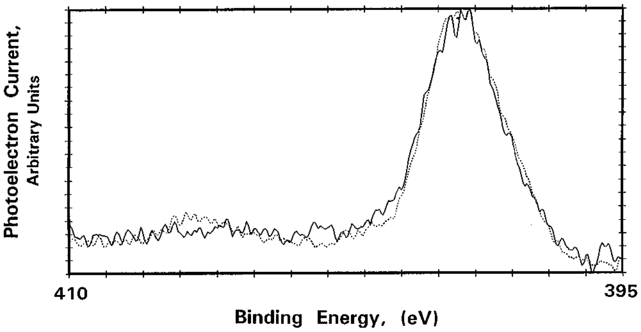

Figure 3. N(1s) spectra from PANI-EB coated glass: (a) room-temperature dried (solid line); (b) 165 °C dried (dotted).

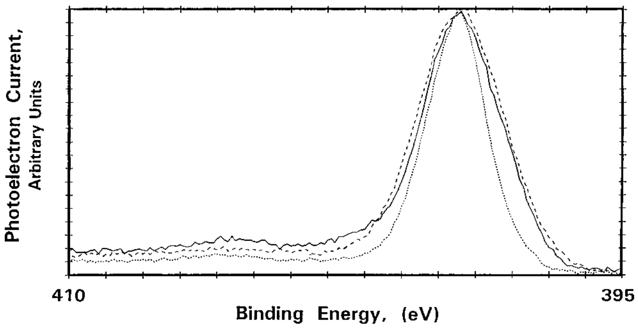

Figure 4. N(1s) spectra from PANI-EB coated CRS: (a) room-temperature dried (solid line); (b) heated to 165 °C in the spectrometer vacuum chamber (dotted line); (c) heated to 165 °C in laboratory air for 8 min (dashed line).

The vacuum environment of the XPS analysis chamber does not in itself cause the reduction of PANI-EB to PANI-LEB: the N(1s) XPS line width of a PANI-EB coating on glass was essentially unchanged when the sample was heated from room temperature to 190 °C.

Figure 3 illustrates a repeat of the above experiment, however with the PANI-EB coated onto glass. In this case there was no difference between the N(1s) spectra of the room-temperature and 165 °C dried samples. Both curves, room-temperature (dried, solid line, Figure 3a) and 165 °C (dried, dotted line, Figure 3b) show the same general form as observed from the room-temperature coating on CRS in Figure 2. The sample on glass had an amine/imine ratio of 2.9. This result demonstrates the greater reduction of the PANI-EB when in contact with CRS compared to glass. High-temperature drying of PANI on glass resulted in chemical oxidation of the PANI surface, as evidenced by the formation of a 405.9 eV peak. There was no evidence of change in oxidation state of PANI on glass with high-temperature treatment, as there was for PANI on CRS.

N(1s) XPS data for PANI-EB/NMP solution dip coated CRS are shown in Figure 4 (a, room-temperature dried, solid line; b, heated to 165 °C in the spectrometer vacuum chamber, dotted line; c, heated to 165 °C in laboratory air for 8 min, dashed line). The room-temperature sample (Figure 4a) is very similar to Figure 2a, showing a similar amine/imine ratio indicating reduction of PANI in contact with CRS. With in vacuo heating to 165 °C, (Figure 4b) the amine/imine peak area ratio increase to ∼9, consistent with more extensive reduction of PANI-EB to PANI-LEB by the steel. After these measurements, the sample was removed from the vacuum chamber, heated in the laboratory atmosphere to 165 °C for 8 min, cooled, and then reintroduced into the XPS. The N(1s) spectrum (Figure 4c) demonstrates that PANI returned to the state of the as-deposited air-dried film (Figure 4a). We understand this to indicate that the PANI-LEB, even as a coating on steel, can be oxidized by air to PANI-EB. Reduction of the polymer by steel can be reversed by air-oxidation.

FTIR Results. The diffuse reflectance FTIR spectra of undoped, solvent-free, polyaniline powder sample were as expected based on the discussions of Milton and Monkman.[16] Reversible temperature-dependent changes in numerous vibrational modes were observed: 3280 and 3166 cm^{-1} N−H stretch, 1600 and 1516 cm^{-1} ring modes, 3052 and 3030 cm^{-1} aromatic C−H stretch modes, and the C−N stretch (1322 cm^{-1}) mode. Water in this material disappeared upon heating to 50 °C for 30 min.

The intensity of the N−H stretch H-bonding 3280 cm^{-1} peak decreased significantly as a function of temperature. The 3166 cm^{-1} mode assigned to a quaternary-like nitrogen/hydrogen stretching mode decreased in intensity together with the 3280 cm^{-1} mode. The temperature dependent change in these modes indicates the rupture of intermolecular H-bonding.

The peak heights for the 1600 and 1516 cm^{-1} aromatic modes were measured above a linear background. The peak height ratio was found to be unity from room temperature up to 120 °C, after which the value decreased to 0.93, at 200 °C.

The C−N stretch mode (aryl secondary amine) was quite broad, and found to shift to lower energy as the temperature increased. Curve fitting was employed to find the centroid of the main component under the broad absorption. The as-prepared room-temperature sample has a peak position of 1315.1 cm^{-1}. Peak position moved consistently lower to a value of 1301.0 cm^{-1} as the temperature was increased to 200 °C. We propose that this red-shift of C−N stretch energy also reflects lower interchain H-bonding at elevated temperature.

While at 200 °C, the sample was exposed to air for 30 min. The sample was then allowed to cool to room temperature under air. The nitrogen purge within the IR spectrometer sample compartment was reestablished prior to collection of a new spectrum. The principal differences between FTIR spectra collected at 200 °C under nitrogen and at room temperature following air exposure at 200 °C reflect the temperature-dependent reversible interchain H-bonding, evident in N−H absorptions (2500−3500 cm^{-1}). No absorptions suggesting oxidation of the PANI-EB were observed.

Adhesion Test Results. Tape pull testing of PANI-EB coated on CRS demonstrated that high-temperature treatment improved the adhesion of polyaniline to steel. For samples which dried at ambient temperature, the tape pull resulted in removal of approximately 12−25% of the coating; for samples cured at 150−200 °C, tape pull removed 0−1% of the coating.

Discussion

XPS Data. The XPS data presented here indicate that a room-temperature coating of PANI-EB on steel substrate is reduced to PANI-LEB. The reduction is an indication of the inherent capability of PANI to participate spontaneously in electron exchange with conducting materials of appropriate electrochemical potential. The reoxidation of PANI at the surface does occur in ambient air at a very low rate.[13] Increasing the temperature of the CRS/PANI sample increases rate of oxidation of PANI-LEB to EB. In the case of a CRS/PANI sample dried at high temperature in air, the oxidation of PANI is rapid, producing a thin film of PANI in an oxidation state higher than that of the polymer applied to the steel. We note that heating a glass/PANI sample in air did not have the same oxidation effect, suggesting the need for an electrochemical partner, or thermal conductor, to facilitate the migration of charge. When heated in air, the glass/PANI sample suffered chemical oxidation, evidenced by nitro functionality at 405.9 eV in the N(1s) XPS. The apparent cooperation between steel and PANI, which leads to oxidation of PANI to a state above the air-stable state of the neat polymer, may be indicative of reaction of iron with oxygen to form a passivating oxide.

Heating a PANI-EB coating on steel to 165 °C in vacuo enhanced electron exchange between PANI and CRS, evident in the XPS data as essentially complete reduction to PANI-LEB. This is the likely result of improved metal−polymer electrical contact; thermal analysis has indicated[10] that neat polymer softens above ca. 150 °C.

The spectral resolution of amine and imine chemical states in XPS data is higher for the neat PANI pellet (Figure 1) than for PANI films on steel or glass (Figures 2−4). Peak broadening results from structural disordering in solution cast films;[17] nitrogen line widths in the PANI coatings are ca. 50% greater than those in the neat pellet prepared from the recrystallized solid.

The XPS technique observed to a sample depth of approximately 5 nm, roughly 0.1% the thickness of the coating. We propose that chemical changes evident at the external surface had been transferred throughout the volume of the coating. Therefore, in our view, these observations of changes in polymer oxidation state indicate charge storage and transfer capacity of undoped, “nonconducting” PANI.

Suggested structures for the 401 and 402.5 eV XPS peaks have been given in the literature. The feature at 401 eV has been attributed to surface oxidation products by Kang, although he also mentions the possibility of protonated imine nitrogens.[13] The imine is thought to be more prone to protonation than the amine. The charge model presented by Siegbahn[18] supports the protonated imine assignment, predicting a N(1s) binding energy of ca. 400.9 eV for this structure.

In our work, the 402.5 eV peak appears only in cases where the PANI was exposed to high-temperature air. While this binding energy is lower than that typical of nitrogen oxides, the evidence suggests an oxygen-containing group of some sort. In the work of Kang

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[16] Milton, A. J.; Monkman, A. P. *J. Phys. D: Appl. Phys.* **1993,** *26,* 1468.

[17] The PANI pellet was comprised of material crystallized from solution following synthesis. The dissolution of the PANI into NMP disrupts this local crystalline order resulting in broader photoelectron data from the solution deposit. Beard, B. C.; Sandusky, H.; Elban, W. *Surf. Interface Anal.* **1993,** *20,* 140.

[18] ESCA, Atomic, Molecular and Solid State structure studied by means of Electron Spectroscopy; Siegbahn, K.; Nordling, C.; Fahlman, A.; Nordberg, R.; Hamrin, K.; Hedman, J.; Johansson, J.; Bergmark, T.; Karlsson, S.-E.; Lindgren, I.; Lindberg, B. Nova Acta Regiae Societatis Scientiarum Upsaliensis, Ser IV, Vol 20, 1967; p 108.

examining $HClO_4$-doped PANI,[19] the 402.5 eV peak grows preferentially to the 401 eV peak, as the acid concentration is increased from 0.01 to 1 M. However, with 1 M HCl, a strong non-oxidizing acid, the 402.5 eV peak is much less intense, suggesting the presence of oxygen in the structure leading to the 402.5 eV peak. A diaryl *N*-oxide, which possesses quaternary resonance structures, may be a possible assignment for this peak. Binding energy estimations for a diaryl *N*-oxide by the Sidgbahn charge model suggest ca. 402.0 eV.

FTIR Data. We observed systematic changes in the FTIR spectra of a powder sample of polyaniline-emeraldine base heated to ca. 200 °C under flowing nitrogen gas. The specific modes that showed variation were the H-bonded N−H stretch, the aromatic C−H stretch, the 1600 and 1516 cm^{-1} ring modes, and the C−N (aryl secondary amine) stretch. In combination, the alteration of these modes suggests the loss at elevated temperature of interchain association of the polymer. The extent of these changes were found to be progressive with increasing temperature and/or time and were found to be partially reversible upon cooling the sample. Physical changes anticipated in response to the loss of interchain association would include a softening of the polymer. Improved mechanical and electrical contact between the polymer and the metal substrate would account for enhanced reduction/oxidation chemistry and improved adhesion between PANI and metal.

Conclusions

Data presented in this work indicate electrochemical interaction between steel substrate and a polyaniline coating, a phenomenon that may lead to protection of steel against corrosion. Using XPS to observe changes in the oxidation state of the polymer, we find that, in the absence of oxygen, steel reduces PANI-EB to PANI-LEB, whereas in the presence of oxygen, PANI-EB on steel is oxidized to a state higher than that of the polymer in air but not in contact with steel. Each of these chemical changes, the reduction of PANI by steel in vacuo and the oxidation of CRS/PANI in air, occurs more rapidly at elevated temperature.

Pellets of neat chemically prepared PANI-EB gave a nitrogen XPS spectrum which indicated the presence of both amine and imine nitrogen. PANI-EB applied as a thin film on cold rolled steel was reduced, as evidenced by the loss of imine nitrogen relative to amine. A similar film on glass also showed an increase in amine nitrogen, but to a significantly lesser degree. The CRS/PANI film heated in the vacuum chamber of the XPS spectrometer was essentially fully reduced, presumably by the steel substrate. The PANI was found to recover its original air-exposed oxidation state after being heated in air for 8 min at 165 °C, demonstrating redox recycling of PANI in contact with steel and air.

CRS/PANI samples heated in air showed a significant increase in the imine nitrogen relative to amine nitrogen. Additional XPS features appeared at 402.5 eV, arising from a partially oxidized amine nitrogen. We attribute a peak at ca. 405.9 eV in the N(1s) spectrum of heat-treated PANI on glass to nitro groups formed by chain scission. The absence of electron exchange between substrate and PANI in this case, we suggest, leads to chemical oxidation of the polymer.

The FTIR data measured on PANI powder not in contact with steel are consistent with thermal analysis[10] in suggesting gradual irreversible changes in the polymer after excursions to elevated temperature. FTIR data are consistent with decreased interchain H-bonding at elevated temperature. We note that mechanical adhesion of the polymer to steel is improved with softening of PANI at higher temperature.

Data presented in this paper provide information relevant to the reported ability of PANI to protect steel from corrosion. The capacity of steel to reduce PANI in the absence of oxygen and the enhanced oxidation of PANI coated steel in air at high temperature are consistent with early[3] and recent[6,7] claims that PANI can assist the passivation of steel. The tendency of engineering metals to react with oxygen to form oxide products is evident everywhere. The possibility that an organic coating may assist formation of a stable adherent oxide[6,7] is extremely important and merits further investigation. Data presented in this paper demonstrate spontaneous electrochemistry between steel and polyaniline which is changed in the presence of oxygen. We are presently investigating the oxide formed on PANI-coated steel.

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(19) Neoh, K. G.; Kang, E. T.; and Tan, K. L. *Polymer* **1993,** *34,* 1630.