

Polyaniline, a Corrosion Inhibitor for Steel: a Mechanistic Study using Video Microimages

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We used a videomicroscopy during conventional electrochemical measurements to ascertain the mechanisms whereby coatings containing polyaniline inhibit the corrosion of steel surfaces. The polyaniline (PANI) coatings were prepared as either a dispersion consisting of PANI and cyclohexanon, or PANI dispersion blended with various ratios of epoxy. We observed that color of the PANI coatings changed during a corrosion test in 1N NaCl solution, from the green emeraldine salt at the beginning to blue or pale yellow. The cyclic voltammogram of the dispersion coatings was basically similar to a pure PANI coating. The color change and the variation of open circuit potential (OCP) differed with the types of dispersion systems. The mechanism of inhibition of corrosion by PANI was investigated based on the result of the electrochemical measurements and close examination of the color changes in the video microimages during corrosion.

Keywords : polyaniline (PANI), dispersion, coating, corrosion inhibition, video micro image

1. Introduction

Corrosion can be explained as electrochemical attacks on metal surface that cause deterioration of the surface and of the structural properties of the metal itself. Thus, protecting the surface of metals has been a major concern for industries.

Growing environmental concerns about the use of heavy metals in formulating coatings to prevent corrosion has led to a new strategy employing electronically conductive polymers. Polyaniline (PANI) is one of the polymers that have been most intensively investigated as a prospective anticorrosive material.¹⁾ It is now generally accepted that the strong passive surface and active electronic barrier afforded by coatings containing PANI can protect metal surfaces. Many previous works showed the positive anti-corrosive behavior of PANI on iron,^{2),3)} carbon steel,⁴⁻⁷⁾ stainless steel,⁸⁾ aluminum,^{6),9)} and copper.¹⁰⁾ However, the mechanism of corrosion inhibition was not clearly demonstrated due to the complexity of the chemistry and electrochemistry of PANI.⁴⁾ Different results were obtained from one investigation to another because of the many different methods applied in preparing PANI coatings on metal surfaces, and of the inherent randomness of

corrosion phenomena.

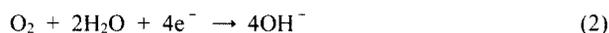
PANI belongs to a class of conductive polymers that can be differentiated from one to another by its oxidation states and doping levels. A well-known emeraldine salt (ES) can be identified by its green color. Pernigraniline is a fully oxidized state observed at very high potential that is sky blue. Undoped PANI also is blue in color, similar to pernigraniline. A fully reduced state of PANI, called leucoemeraldine, is pale yellow. Usually, the different states of PANI coexist during electrochemical polarization or synthesis.²⁾

A method of adding pH indicators to paints recently was adapted to locate anodic and cathodic sites.^{11),12)} Isaacs *et al.*¹³⁾ used video microimages to demonstrate color changes in a gel containing a broad-range pH indicator when pitting corrosion took place locally on aluminum surface.

The anodic reaction occurring at a locally corroding site of metal surface can be written as



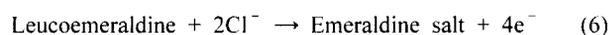
The cathodic reaction of oxygen reduction takes place simultaneously at the surrounding surface



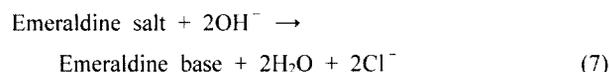
The electrons produced by oxidation of the metal at a corrosion site flow to the surrounding metal surface and are consumed by an oxygen-reduction reaction. If there is a PANI coating on top of metal's surfaces, then the electrochemistry during localized corrosion could occur differently. It was postulated that an electronically conductive polymer stabilizes the potential of the metal in a passive regime, maintaining a protective oxide layer on the metal. Oxygen reduction on the polymer coating is thought to replenish the polymer's charge consumed by metal dissolution, thereby stabilizing the potential of the exposed metal in the passive regime and minimizing the rate of metal dissolution.¹⁴⁾ Fig. 1 illustrates the electrochemistry occurring at a metal/PANI coating system in an aqueous solution. The following redox reactions take place simultaneously both at metal/polymer interface and at polymer/solution interface. At metal/polymer interface, the redox reaction can be expressed as



when PANI is an HCl doped emeraldine salt. The oxidized metal ions can be converted into a protective oxide layer, incorporating oxygen diffused into the coating. At the polymer/solution interface, the following redox reaction can compensate for the consumption of an electron in the PANI coating



The emeraldine salt of PANI can be deprotonated in the basic environment forming on the surface where the oxygen reduction reaction takes place.



Gašparac and Martin⁸⁾ followed the Open Circuit Potential (OCP) of PANI-coated stainless steel in 1 M H₂SO₄ solution. The OCP recovered to a very positive potential relative to the bare metal after an initial sharp decrease. They suggested that this was due to passivation of the underlying stainless steel surface by the PANI coating; they concluded that the entire metal surface did not have to be covered with protonated doped PANI emeraldine salt to achieve passivation, as suggested by

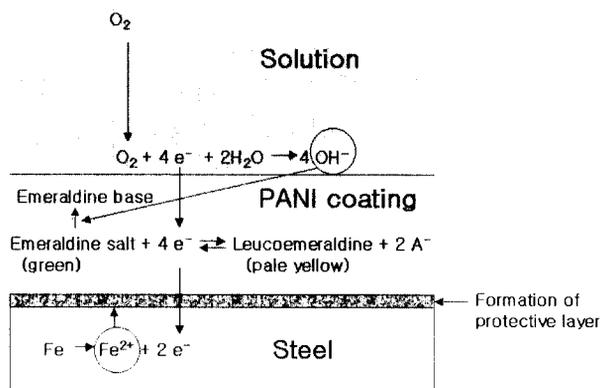


Fig. 1. Electrochemistry occurring at iron/PANI coating in an aqueous corrosive solution

others.^{5),7)} However, Bernard *et al* studying an electrochemically deposited PANI coating on iron judged that a good quality PANI coating is very important for protecting iron surfaces efficiently in acidic sulfate solutions.²⁾

In this work, we employed video-microscopy to observe color changes in PANI coatings during conventional measurements of electrochemical corrosion, such as measurements of open circuits and polarization, and correlated our observations from video microimages with these results. We anticipated local color changes in the PANI coating on a metal surface during corrosion because this conductive coating reveals various colors, depending upon local chemistry. The materials that we used to make coating were the following: (1) PANI dispersions in an organic solvent, cyclohexanone that can be relatively easily evaporated compared with N-methylpyrrolidinone (NMP), and provides a fairly uniform coating, and, (2) PANI dispersion/epoxy blend with various mixing ratios. We also used different curing times for the coatings to understand the effects of the coating on the formation of a protective passive layer.

2. Experimental

2.1 Synthesis of polyaniline

Aniline solution was made by adding 20 mL of aniline (Shinyo Pure Chemical Co., GR reagent) to 300 mL of 1 M HCl (Yakuri Pure Chemical Co., GR reagent) solution. The oxidant solution was prepared by dissolving 11.5 g (approximately 0.05 mol) of ammonium peroxydisulfate (Shinyo Co., GR reagent, (NH₄)₂S₂O₈) in 200 mL of 1 M HCl solution. Both solutions were pre-cooled to ~0°C in an ice bath. The aniline solution then was placed in a 1 L beaker or a 750 mL Erlenmeyer flask with a magnetic bar, and placed in an ice bath on a magnetic

stirring plate. The oxidant solution was added within 1 minute to the aniline solution while stirring it constantly. The mixture then was stirred in an ice bath for about 2 hr.

After this, a dark green precipitate was obtained by filtering the mixture through a Buchner funnel using a water aspirator. The precipitate was washed in an excess of 1 M HCl, and dried in an oven. The emeraldine salt powder of PANI was finally obtained by grinding up the small pieces of dried precipitate.

2.2 Preparation of PANI dispersion and PANI/epoxy blend

The PANI emeraldine salt obtained in this work was insoluble in most solvents. Some investigators used a base form of PANI that would dissolve in organic solvents such as NMP, THF, and DMSO; other investigators prepared dispersions as coating materials.

We made a dispersion of PANI from the powdered emeraldine salt. Dry scraps of PANI were ground in a ball mill into a powder that then was reduced for 40 hr to a much finer powder in a micro-milling machine (Fritsch Co., Model No. Pulverisette 7). The fine powder (0.05 g) was added to approximately 16 g of cyclohexanon (Waco Co., WR reagent) together with a small amount (0.01 g) of a polymer surfactant, Hypermer LP-1 (ICI Co.). The mixture was stabilized in micro-milling machine for 20 ~ 60 hr. A detailed description of our method will be published soon.¹⁴⁾ The stabilized dispersion maintained its dark green color.

PANI/epoxy blends were prepared by mixing the PANI dispersion and epoxy (Epo-Tec 396, single component epoxy, Epoxy Technology Co.) with the ratios of 1:1, 2:1, 4:1, up to 8:1. The PANI/epoxy blend coating was applied to metal surface immediately after blending. The drying time for the dispersions and blends varied between 20 and 40 min, depending on the thickness of the coating, but did not exceed 1 h in air at room temperature.

2.3 Video microscopy observation and electrochemical measurements

A carbon-steel (c-1010, 1 x 1 cm²) substrate was mounted on a cold cured epoxy resin and was abraded down to 1200-mesh silicon-carbide paper, and washed with methanol and then distilled water. The PANI dispersion or PANI/epoxy blend was applied drop-wise on the clean steel surface, and the coating cured in air at room temperature. To investigate the passivating effect of the PANI coating on the steel surface, the coated specimen was allowed in air for controlled durations, such as 1 hr after application, 24 hr, 48 hr, and so on. We examined

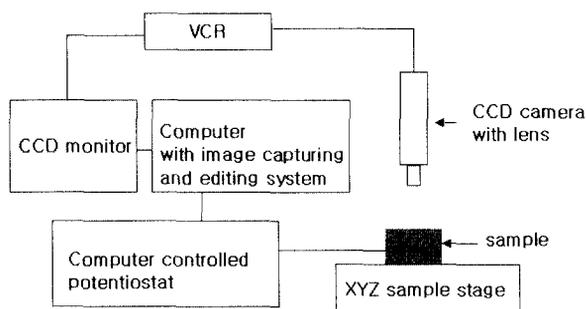


Fig. 2. Schematic diagram of electrochemical video microscopy system

the corrosion behavior of the specimens with different curing periods in 1 M NaCl solution.

The coated specimen was masked by polyester tape (3M Co., type no. 5) with a window area of few mm², depending on the magnification of video camera. The open-circuit potential of the uncoated carbon steel, the PANI dispersion coated steel, and PANI/epoxy blend coated electrode then was monitored against a saturated calomel electrode (SCE) or an Ag/AgCl reference electrode using an EG&G 273A potentiostat connected to a personal computer. Video images were also stored on a videotape using a SONY VCR. Fig. 2 is a schematic diagram of the instruments used for video microscopy and electrochemical measurements.

3. Results and discussion

Fig. 3 shows the OCP of various samples measured in 1 M NaCl solution. As expected, the OCP of the bare steel showed a rapid decrease in the early stages of the corrosion test, but with many fluctuations between the beginning of the test and 2 hr later, which indicate the rate of growth of pits and depassivation of the surface. The decreasing tendency continued to approximately -0.63 VSCE up to 2 hr, and the OCP stabilized up to 5 hr. The OCP then fell again fairly rapidly and reached at a steady state value of -0.73 ~ -0.75 V between 6 hr and 20 hr. The OCPs of the PANI-coated steel electrodes showed some improvement in preventing corrosion the steel surface. The degree of the improvement depended on the curing period in air. The PANI-coated steel electrodes with more than 48 hr immersion had improved corrosion potential compared with that of a 24 hr-treated steel electrode, but almost the same as a 72 hr-treated steel specimen. The PANI coating must remain on the steel surface to maintain these improvements because the OCP of a steel specimen, from which the coating was removed after 48 hr treatment, shows lower OCP values. Table 1 compares the OCP values of different types of specimens,

Table 1. Comparison of the OCP values of different samples

Sample type	OCP value (VSCE)		
	2 hr	6 hr	20 hr
Bare steel	- 0.64	- 0.71	- 0.75
24 hr coating	- 0.57	- 0.65	- 0.68
48 hr coating	- 0.48	- 0.58	- 0.64
Removed 48 hr coating	- 0.60	- 0.68	- 0.71
72 hr coating	- 0.47	- 0.55	- 0.64

showing that the longer the curing time the better are the protective properties of the coatings. We measured the OCP of a 96-hr PANI coated steel specimen; there was no further improvement in anticorrosion properties.

Our observations from the video camera correlate with the OCP results. Fig. 4 shows the images of a bare steel surface during OCP measurement: (a) just after the solution was introduced in the cell, (b) 30 min later, (c) 1 hr later, (d) 2 hr later, (e) 24 hr later, and (f) after cleaning the surface [AW7]. The size of the window that allows the surface to contact the corrosive solution is approximately 5 x 5 mm². During the first 10 min of immersion, the shiny bare steel surface turned to brownish

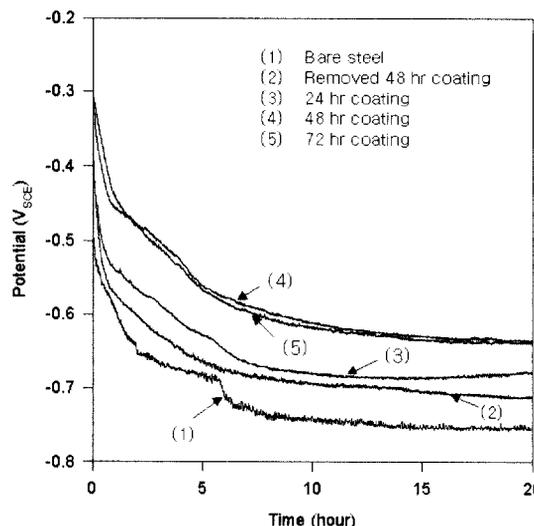


Fig. 3. Open circuit potential of steel electrodes, with various treatments of PANI coating, measured in 1 M NaCl solution

suggesting localized corrosion and delamination. Several large brown spots appeared on the steel's surface within 30 min (Fig. 4 b). Many pits initiated in this brown anodic region in the early stages of the corrosion test. Several dominant pits became bigger between 1 and 2 hr, and

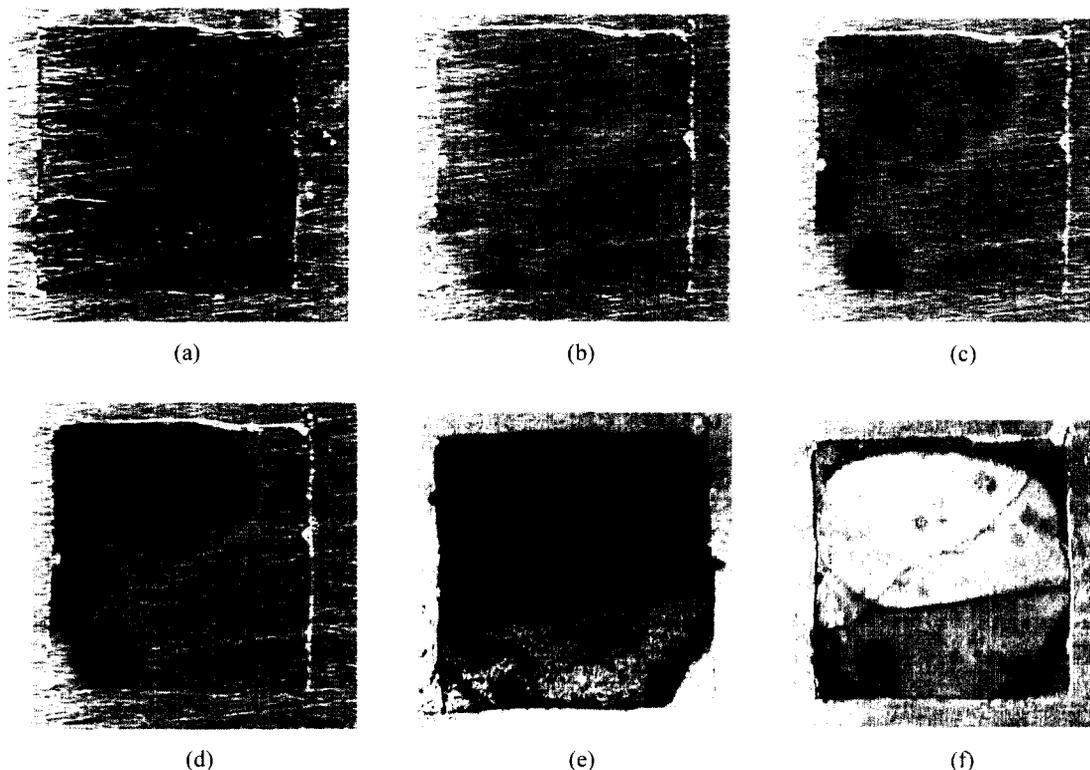
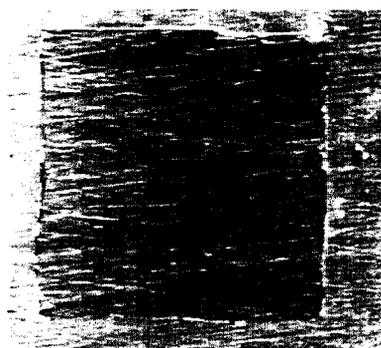
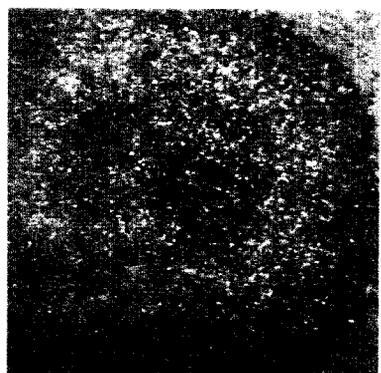


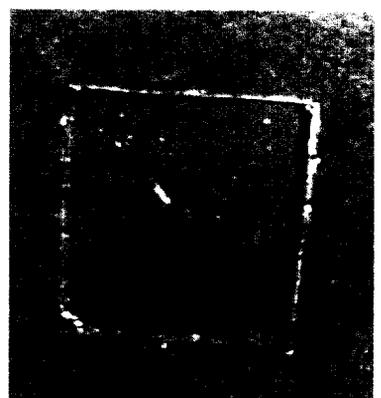
Fig. 4. Video images of a bare steel surface immersed in 1 M NaCl solution at (a) beginning of the experiment, (b) 30 min later, (c) 1 hr later, (d) 2 hr later, (e) 24 hr later, and (f) after cleaning the surface.



(a)



(b)



(c)

Fig. 5. Images of (a) a bare steel surface, (b) 24 hr PANI-coated steel surface, and (c) 24 hr PANI-coated steel surface after the coating was removed.

crevices also were observed at the tape-covered edge of the sample. The OCP stabilized around at -0.7 V after 5 hr. After 24 hr of the corrosion test, thick brown corrosion precipitates largely covered the steel surface. We then removed the precipitates with distilled water, and observed the steel surface (Fig. 4 f); several big spots corresponding to pitting corrosion appeared in the image.

The drop-wise coating process of the sample was moni-

tored through video microscope. One drop of the dispersion spread to approximately $0.7 \sim 1$ cm diameter. The PANI dispersion was completely dried in air at room temperature between 20 ~ 40 min, depending on its thickness. A PANI-coated steel specimen was a brighter green than the original material after drying because light was reflected by the shiny steel surface. However, the coated sample lost the bright green color soon afterwards became dark green or reddish green within 1 hr in air. This green was different from the usual color of an emeraldine PANI film formed on a glass slide, which might be due to a change in the steel's surface under the coating. To examine the steel's surface, we removed the PANI coating with a type no. 5 tape (3M Co.), washed the surface with distilled water and methanol, and dried it in air at room temperature. We found that the original shiny surface had become tarnished to brown after ~ 1 hr of covering with the coating. The degree of tarnishing also differed with the duration of coating. Fig. 5 shows the images of (a) a bare steel surface, (b) 24 hr PANI-coated steel surface, and (c) 24 hr PANI-coated steel surface after the coating was removed. The chemical composition of the layer was reported as Fe_2O_3 ,¹⁵⁾ and Fe(dopant) complex layer.⁷⁾ Thus, the image taken after 24 hrs aging PANI coated on steel shows that the color of the PANI coated surface itself partly turned to a golden brown. The color of the layer formed on the steel surface under the coating was different, being a mixture of brown, blue, and green. Our video microscopic observations verify that the PANI coating induces the development of a protective layer on the steel's surface while drying in air.

Fig. 6 shows the video images of the steel specimen with a 1 hr PANI coating immersed in 1 M NaCl solution. Fig. 6 (a) is the image of the PANI coating after 10 min into the corrosion test, (b) after 30 min of immersion, (c) after 2 hr, (d) after 24 hr, and (e) image of the steel surface after removing the coating at the end of corrosion test at 24hr[AW8]. The area of the window was approximately 5×5 mm². The dark green PANI coating under the transparent masking tape clearly indicates that emeraldine salt was coated on the steel surface.

When the specimen was immersed in the corrosion solution, the color of the coating began to change. Fig. 6 (b) is the image of the coating after 10 min, showing a large area of light green and a small area of dark green. There are several very tiny dark-green spots within the light-green area. This distinguishable color change became more obvious (Fig. 6 b and c); crevice corrosion at the edge of the tape was apparent, as shown in Fig. 6 (c). From the video microimages we did not discern any dominant pitting sites in the PANI-coated specimen until

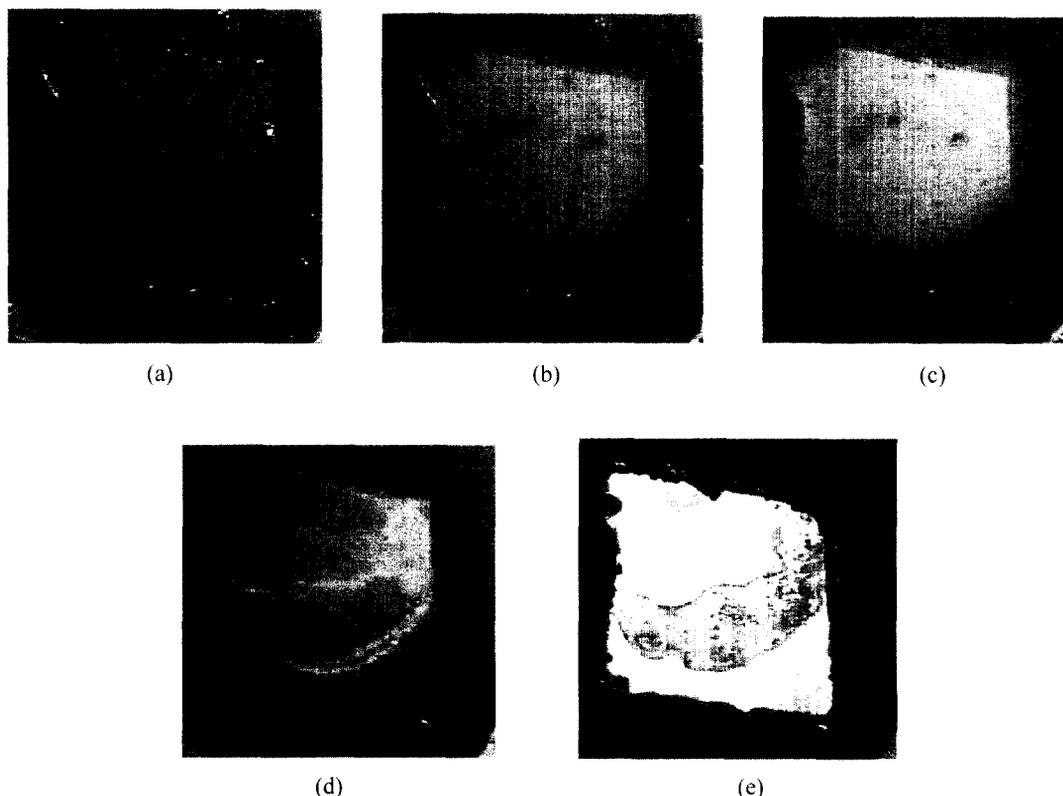


Fig. 6. Video images of 1 hr PANI coating (dried in air for 1 hr)/steel surface immersed in 1 M NaCl solution (a) 10 min later, (b) 30 min later, (c) 2 hr later, (d) 24 hr later, and (e) after removing the coating.

after 5 hours, one pitting site with two sites of crevice corrosion and breakdown of the coating were apparent. After breakdown of the coating, the mechanism of corrosion seemed to change. The area exposed to the solution now can serve as a cathodic site and the remaining part of the surface as an anodic site. Fig. 6 (d) shows the image after 24 hr of test. However, the image under the coating (Fig. 6 (e)) reveals that an anodic metal oxidation reaction had taken place at the middle of the steel's surface, and other parts of the surface acted as cathodic sites. Many small pitting sites were visible in the anodic area.

Correlating our video microscopy observation and the OCP behavior indicates that local corrosion can occur under the 1 hr PANI-coated steel sample, but even if the coating was broken down after several hours in the corrosive solution, no big pits developed. The light-green color of the PANI can be interpreted as consequence of the reduction of the emeraldine salt to leucoemeraldine due to an anodic oxidation reaction under the coating. Therefore, the PANI coating above the corrosion sites was reduced to leucoemeraldine, and this, in turn, was subsequently reoxidized to emeraldine salt, which turned into the base form (de-doping) in basic environments. The basic environment occurred from oxygen reduction

reactions at the cathodic surface. Consequently, the PANI coating did not significantly inhibit corrosion after 1 hr, and its quality was not sufficiently reliable as a corrosion protective coating. We observed that the coating had broken down in many other repeated experiments within several hours.

Fig. 7 has the images of PANI-coated steel specimens after 24 hr in the corrosive solution. The color of the 1 hr exposed steel surface was brown corresponding to the color of iron oxides. However, the color of 24 hr unexposed PANI-treated steel surface was blue-green, but after 24 hr of the corrosion solution it became bright yellow (gold) when it was covered with corrosion products, and dark blue after removing them, as shown in Fig. 7 (b) and (c). This finding indicates that the protective layer formed on steel surface by the PANI coating contains some of the conducting polymer; however, it seems not to delay or inhibit the anodic reaction on the steel's surface, but to play a role in the uniform dissolution of the steel surface. Fig. 7 (d) shows a relatively clean uniform dissolution at anodic areas with several very small spots corresponding to pitting sites. The protective layer also is very porous, so that dissolved corrosion products on the steel surface had diffused out of the layer and an

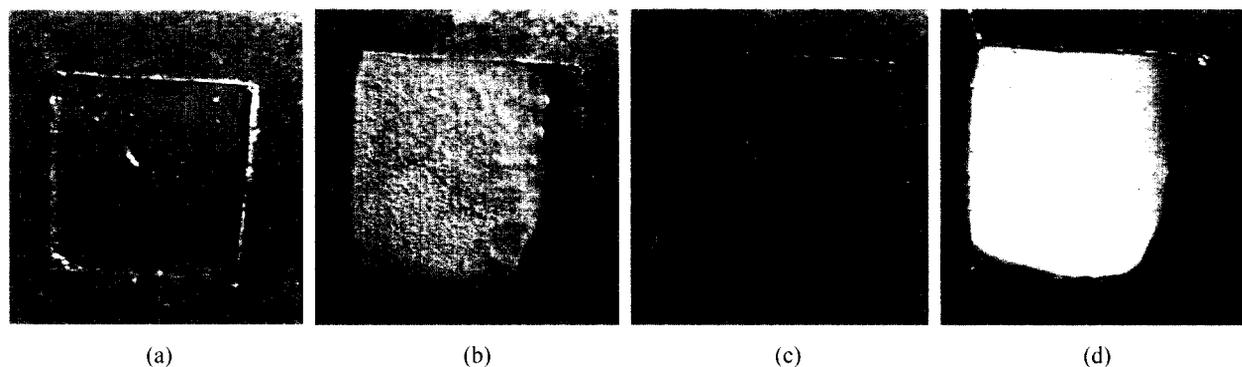


Fig. 7. Video images of 24 hr PANI-coated steel surface at (a) beginning of corrosion test, (b) 24 hr later, (c) after removing the covering corrosion products, and (d) after removing the protective layer.

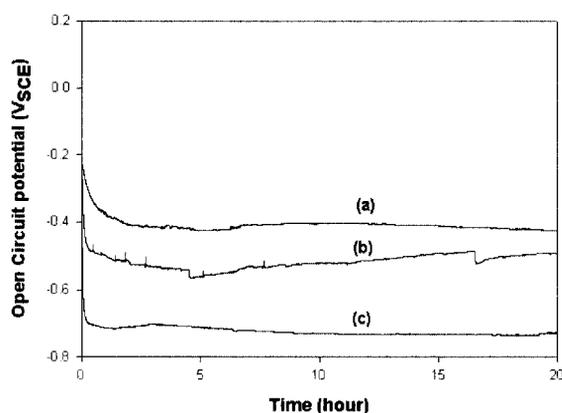


Fig. 8. The OCP of various sample specimens measured in 1 M NaCl solution: (a) a PANI/epoxy (1:1) blend coated steel, (b) PANI/epoxy (2:1) blend coated steel, and (c) 1 hr treated PANI only coated steel specimen.

insoluble corrosion product was formed on top of the layer. Similar phenomena were observed for the 24 hr PANI-coated steel specimen.

The OCP results of the PANI/epoxy blend coatings with various ratios of PANI to epoxy also showed corrosion inhibiting characteristics, and the greater the epoxy content, the higher the OCP potential. Fig. 8 (a) and (b) shows the OCP of PANI/epoxy blend coated steel with the ratios of 1:1 and 2:1, respectively, and (c) is 1 hr treated PANI only coated steel specimen. The color changes were different from those of PANI only coating. The PANI/epoxy (1:1) blend was initially green, but most parts turned to blue. A change in the blend coating from green to round yellow or brown locally was not observed clearly, but seemed to be manifest as very tiny pale yellow spots over the coating. After several hours of immersion in 1 M NaCl solution, the blend coating turned to blue and its edge became brown, due to crevice corrosion at the taped edge. This finding indicates that PANI/epoxy

blend coating provide better protection against corrosion for the steel surface than do the non-blended PANI coatings. However, a high concentration of epoxy may reduce PANI's beneficial effect of conductance in the coating. We plan to find an optimum ratio of epoxy in the conducting polymer coating. The OCP results and interpretation of impedance data will be discussed in a later paper.

4. Conclusions

1) PANI coatings increase the open circuit potential of the steel to a certain extent depending on their curing time in air. A suitable curing time of between 48 ~ 72 hr effectively protects steel surfaces from corrosion in 1 M NaCl.

2) Video microscopic observation showed that the protective layer on the steel surface under the coating contains some PANI molecules.

3) The color of PANI coating on the steel surface changed partly from green to light green at the early stages of the corrosion experiment, and finally becoming entirely blue at 24 hr. This finding indicates that the emeraldine salt of PANI was reduced during the early stages of exposure and then re-oxidized. The re-oxidized emeraldine salt of PANI was transformed to a base form of PANI due to the basic environment generated by the cathodic oxygen reduction reaction taking place on the surface. PANI/epoxy blend coatings better protect steel surfaces against corrosion than do non-blended coatings. The optimum ratio and other influences of the epoxy content in the coating should be investigated further.

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