

## Electrochemistry and Corrosion Characteristics of Polyaniline Dispersion Coating for Protection of Steels

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**Abstract.** Processible polyaniline (PANI) dispersions consisting of polyaniline micro-particles, cyclohexanone, and a polymeric surfactant were prepared in a micro-milling machine with various mixing conditions. The electrochemical properties of the dispersion film coated on Pt electrode were investigated by cyclic voltammetry (CV). The electrochemistry of the PANI dispersion coatings was basically similar to a pure PANI coating based on the results of CV. The results of polarization measurements and open circuit potential measurements carried out in 3 wt.% NaCl solution showed increase in corrosion potential when the PANI dispersion coatings applied on steel surface. Variation of open circuit potential (OCP,  $V_{oc}$ ) of the dispersion coating/steel electrodes was observed, which differed with milling conditions. The results demonstrated practical use of the conducting polymer dispersion as a coating material for corrosion prevention of steel.

**초 록:** 폴리아닐린 분말과 고분자 계면활성제, cyclohexanone 용매를 micro-milling 장치내에서 분산시켜 (m 입자 크기를 갖는 가공용이한 분산액을 제조하였다. 분산액을 백금 전극 위에 코팅하여 얻은 분산박막의 전기화학적 특성들은 순환전압전류법(CV)을 이용하여 조사하였다. CV의 결과에 의하면 폴리아닐린 분산박막이 순수한 폴리아닐린 박막과 유사한 전기화학적 특성을 갖는 것으로 나타났다. 3 wt.% NaCl 용액에서 수행한 분극실험과 열린회로전위 측정 실험에서는 PANI 분산액을 철표면에 코팅하면 부식전위가 증가하였다. 분산박막/철 전극의 열린회로전위값(OCP,  $V_{oc}$ )이 분산액의 제조 조건에 따라 변화가 있음을 관찰하였다. 이러한 결과들은 본 연구에서 사용한 전도성 고분자 분산액이 철의 부식방지코팅물질로서 유용성을 갖고 있다는 것을 보여주고 있다.

**Key words :** Polyaniline dispersion, Cyclic voltammetry(CV), Polarization measurement, Open circuit potential, Corrosion prevention.

### 1. Introduction

Corrosion and corrosion prevention of steels have long been an important research subject among the scientists in various scientific and engineering areas because corrosion of steels causes not only a loss of hundreds billion dollars annually, but threat security of today's highly civilized society established based upon use of steels. Corrosion prevention can be achieved by coatings and conversion layers, which contain toxic and harmful materials to global environment. Growing demands about clean environment and healthy society have led to a new strategy employing electronically conductive polymers (ECPs). Since the first report about corrosion prevention of iron using electronically conductive polyaniline (PANI) coating by Mengoli *et al.*<sup>(1)</sup> in 1981, PANI has become one of ECPs that have been most intensively investigated as a prospective anticorrosive material<sup>(2-20)</sup>.

It is now generally accepted that the strong passive surface and active electronic barrier afforded by coatings containing PANI can protect metal surfaces from corrosion. Many previ-

ous works showed the positive anticorrosive behavior of PANI on iron<sup>(3-7)</sup>, carbon steel<sup>(7,16)</sup>, stainless steel<sup>(16,17)</sup>, and other metals<sup>(11,18-20)</sup>. However, the mechanism of corrosion inhibition was not clearly demonstrated due to the complexity of the chemistry and electrochemistry of PANI<sup>(2,9)</sup>. McAndrew concluded that PANI contributes to the formation of an electrical field at a metal surface, thus restricting electronically the flow of electrons from metal to an oxidant, and forms dense, adherent, low-porosity film that restricts access of oxidants, and causes the formation of protective layers of metal oxides<sup>(2)</sup>. Gašparac and Martin<sup>(17)</sup> followed the Open Circuit Potential (OCP) of PANI-coated stainless steel in 1 M H<sub>2</sub>SO<sub>4</sub> 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 others<sup>(7,10,12)</sup>. 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<sup>(6)</sup>.

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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, so called emeraldine base (EB), also is blue in color, similar to pernigraniline. A fully reduced state of PANI, called leucoemeraldine, is pale yellow. The following is the chemical structure of PANI, the oxidation states of which vary with  $y$  value where  $y = 1$  is leucoemeraldine (reduced form),  $y = 0.5$  is emeraldine (half-oxidized form), and  $y = 0$  is pernigraniline (fully-oxidized form).

In most cases, emeraldine salts with a small dopant do not dissolve in water or general organic solvents. In the other case, undoped emeraldine base could be used to dissolve or disperse only in strong polar solvents like *N*-methylpyrrolidone (NMP) or dimethylformamide, high boiling point and high toxicity. However, these solvents are not acceptable to coating industry<sup>2)</sup>.

Since the work by Armes and Aldissi<sup>21)</sup> in 1989, there have been numerous reports on the preparation of PANI dispersions<sup>22)</sup>. These are produced when PANI is prepared in the presence of a suitable steric stabilizer, usually a water-soluble polymer. Dispersions are composed of colloiddally stable submicro-meter PANI particles dispersed in the aqueous medium. Particles are protected from the aggregation by a surface layer of the attached stabilizer.

In this work, processible dispersions containing sub-micron size particles of PANI were prepared by using mechanical milling, which could overcome restricted use of solvent, and are applicable to coating industry. The electrochemical properties of the dispersion coatings were then compared with the properties of the PANI only coating obtained during chemical synthesis of PANI. Cyclic voltammetry was utilized to illustrate electrochemical redox properties of the coating. Polarization measurements were employed to examine the effect of the coating on corrosion protection. The materials that we used to make coating were the PANI dispersions in cyclohexanon that can be relatively easily evaporated compared with *N*-methylpyrrolidinone(NMP), and provide a fairly uniform coating.

## 2. Experimental

### 2.1. Synthesis of polyaniline and preparation of stable polyaniline dispersions

HCl doped Polyaniline salts were prepared through a well-known method of chemical synthesis. 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 of ammonium peroxydisulfate (Shinyo Co., GR reagent,  $(\text{NH}_4)_2\text{S}_2\text{O}_8$ ) in 200 mL of 1 M

HCl solution. Both solutions were pre-cooled to  $\sim 0^\circ\text{C}$  in an ice bath and then were gradually mixed in a 1 L beaker or a 750 mL Erlenmeyer flask with a magnetic bar. The synthetic vessel was placed in an ice bath on a magnetic stirring plate for about 2 hr. Dark green precipitates were finally 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 fine powders of HCl doped PANI salt were finally obtained by grinding up the small pieces of dried precipitate.

Polyaniline dispersions with various weight ratios (0.5~5%) were then prepared by mechanical milling of the mixture consisting of fine polyaniline salt powders, cyclohexanone (Wako Co., GR reagent), and a small amount of Hypermer 'LP-1' (ICI Co.) as a polymeric surfactant. A planetary micro-milling machine (Model No. P-7, Fritsch Co., Germany) was used for preparation of the dispersion. The mixture was then dispersed in the milling machine for 20~100 hrs with 600~750 rpm of rotating speed. We used a zirconia bowl having 40 mL of its maximum capacity and approximately 10 g of zirconia balls having 2 mm in diameter.

### 2.2. Electrochemical measurement

The electrochemical cell for cyclic voltammetry consists of three electrodes: a working electrode (Pt plate,  $2 \times 5 \text{ cm}^2$ ), count electrode (Pt plate or wire), and a saturated calomel electrode as a reference electrode. The electrolytic solution used for the measurement is 1 M HCl aqueous solution. The working electrode was prepared by either drop-wise coating of the PANI dispersion on a Pt electrode (Aldrich Co.) and naturally formed PANI coating on Pt electrode during chemical synthesis of PANI. The cyclic voltammetric measurements were carried out by scanning potential between 0.2 and 1.0  $V_{\text{SCE}}$  with various scan speeds between 20 and 100 mV/s. Cyclic voltammograms were then plot to compare electrochemical redox properties of the PANI dispersion films with those of the film prepared by an electrochemical method.

A carbon-steel (c-1010,  $1 \times 1 \text{ cm}^2$ ) 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 was applied drop-wise on the clean steel surface, and the coating cured in air at room temperature. 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 hr in air at room temperature.

The coated specimen was masked by polyester tape (3 M Co., type no. 5) with a window area of few  $\text{mm}^2$ . The open-circuit potential of the uncoated carbon steel, and the PANI dispersion coated steel electrode then was monitored against a saturated calomel electrode (SCE) or an Ag/AgCl reference electrode. The open circuit potential was monitored for at least 24 hr. We also observed the electrode surfaces during the open circuit measurements through a color video microscope<sup>23)</sup>. The polarization measurements of an iron electrode coated by PANI dispersion or PANI/epoxy blend were carried out in 3 wt.% NaCl solution saturated with air, which is sim-

ilar to sea water in NaCl content. The measurements were made with a scan rate of 0.2 mV/sec and between 300 mV above and below the open circuit potential of the electrode. Electrochemical measurements were carried out either by Volta Lab PGZ 402 universal pulse dynamic-EIS voltammetry instrument (Radiometer Analytical Co.) or EG&G 273A potentiostat/galvanostat connected to a personal computer.

### 3. Results and Discussion

The PANI dispersions were prepared by mixing PANI particles, cyclohexanone as a solvent, and a small amount of Hypermer as a polymer surfactant into a zirconia bowl for a given duration between 10~100 hr with 600~750 of rotating speed. The products made by this mechanical milling processes resulted in stable dispersion having dark green color. We investigated sizes and densities of PANI particles in the dispersion using an optical microscope. Fig. 1 shows optical microscopic images of the particles in the 0.5 wt.% PANI containing dispersion in cyclohexanone obtained by milling (a) 12 hr, (b) 48 hr with 600 rpm of rotating speed, (c) 48 hr with 750 rpm of rotating speed, and (d) 1 wt.% PANI containing dispersion obtained by milling 48 hr with 750 rpm of rotating speed. Area of the image is approximately  $2.79 \times 3.37 \text{ mm}^2$ . Comparison of the images demonstrated that longer milling time and faster rotating speed resulted in finer and better dispersed PANI particles in the dispersion. We were not able to determine the size of the particles precisely, but could explain them as various sizes of the sub micron particles tangled with each other. The densities of PANI par-

ticles in the dispersion apparently were likely proportional to the PANI contents in the dispersion.

Fig. 2 shows the cyclic voltammograms of PANI only coating (dashed line) on Pt electrode obtained during chemical synthesis and (b) drop-wise coating of the PANI dispersion coating (solid line) on Pt electrode in 1 M HCl aqueous solu-

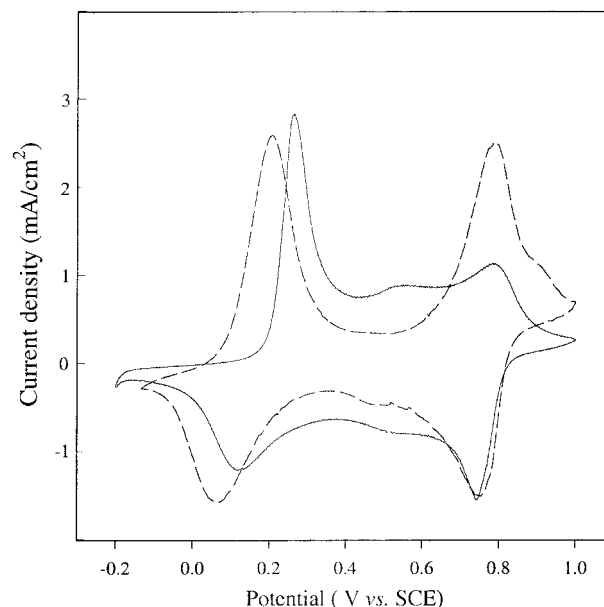


Fig. 2. Cyclic voltammograms of (dashed line) the PANI only coating prepared by chemically synthesized pure polyaniline, and (solid line) the polyaniline dispersion coating (20 hrs milling at 600 rpm) in 1 M HCl solution. Scan rate = 50 mV/s.

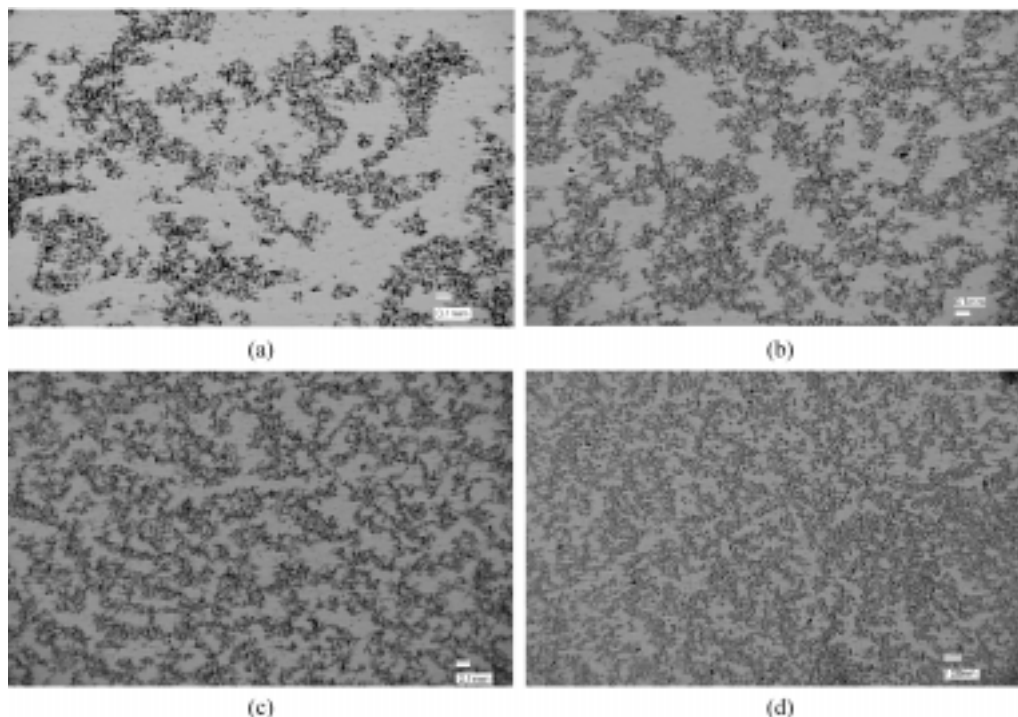


Fig. 1. Optical microscopic images of the particles in the 0.5 wt.% PANI containing dispersion in cyclohexanone obtained by milling (a) 12 hrs with 600 rpm of rotating speed, (b) 48 hrs, (c) 48 hrs with 750 rpm of rotating speed, and (d) 1 wt.% PANI containing dispersion obtained by milling 48 hrs with 750 rpm of rotating speed. Area of the image is approximately  $2.79 \times 3.37 \text{ mm}^2$ .

tion. The coating was obtained from the dispersion made by 50 hr of milling time and 600 rpm of rotating speed. Both voltammograms show two distinctive redox peaks corresponding to transition from fully reduced leucoemeraldine to half oxidized emeraldine to fully oxidized pernigraniline and vice versa. The characteristic redox potentials  $[(E_{pc} + E_{pa})/2]$  of PANI appear at 0.1 and 0.77 V for PANI only coating, and at 0.19 V, and 0.77 V for the PANI dispersion coating (20 hrs milling at 600 rpm). A smaller broad peak at 0.54 V in the voltammogram of the dispersion coating indicates low molecular weight intermediates<sup>24,25</sup> presenting in the coating, that might be produced during milling process. The values of the first and second oxidation peak current densities for the dispersion coating were 2.83, and 1.13 mA/cm<sup>2</sup>, respectively. The relative ratio of the two peak currents was also different from the equal ratio of the two peak values in the pure PANI coating.

We further obtained cyclic voltammograms of the coating made by the dispersion prepared with different milling conditions, and investigated possibility that milling process causes intermediate formation. Fig. 3 shows cyclic voltammograms of the coatings prepared from the dispersions made with (a) 20 hr milling, (b) 50 hr milling, and (c) 100 hr milling at 600 rpm of rotating speed. The  $E_{1/2}$  of the 50 and 100 hr dispersion coatings were observed at 0.23 and 0.28 V, respectively, resulting in shifting of the first oxidation peak toward more positive direction, while the second oxidation peak remained at ~0.77 V for all the coatings without shifting. The small broad peak at 0.54 V was observed for all the coatings, and the amplitude of the peak increased as milling time increased. This result could be a supporting evidence of the earlier statement that the milling process can cause breakdown of the polymer chains and produce segments polymers with low molecular weight.

Fig. 4 shows potentiodynamic polarization curves for (a) bare steel surface and (b) 70 hr cured PANI dispersion coating (50 hrs milling at 600 rpm) on steel surface in 3 wt.% NaCl solution. The coating was cured for 48 hr in air at room temperature. The initial color of the coating was dark green, which is the color of PANI emeraldine salt. The color of the coating was then changed to brownish dark green after 48 hr of curing time. Scan range was between 0.8 and 0.3 V<sub>SCE</sub> and the scan rate was chosen as 0.2 mV/sec. Corrosion potential ( $E_{corr}$ ) of the PANI coated steel positively increased 0.1 V when compared with that of the bare steel. However, the corrosion current of the PANI dispersion coating/steel electrode did not decrease markedly when compared with that of the bare metal electrode. It might indicate that complicate mechanisms of PANI coating for protecting steel surface from corrosion were implied, which should be clarified through further precise investigation.

Fig. 5 shows the open-circuit potentials ( $V_{oc}$ ) of (a) 70 hr cured PANI dispersion coating (50 hrs milling at 600 rpm) on steel surface, (b) 70 hr cured PANI dispersion coating (100 hrs milling at 600 rpm) on steel surface, (c) 70 hr cured PANI dispersion coating (20 hrs milling at 600 rpm) and (d) bare steel in 3 wt.% NaCl solution. This result also demon-

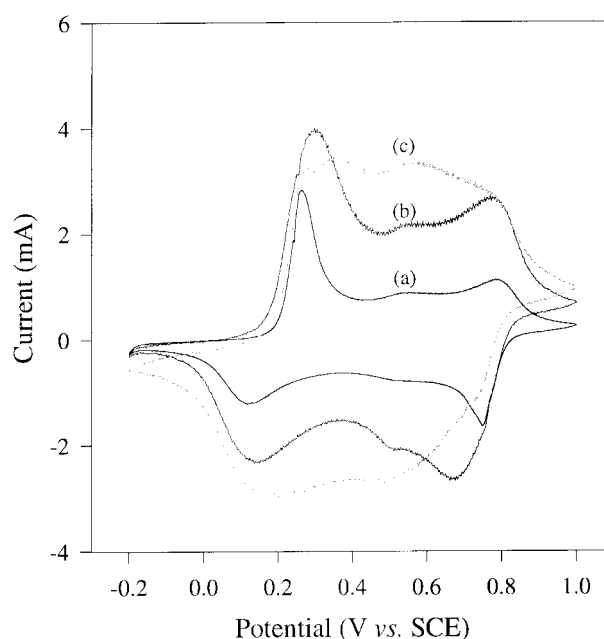


Fig. 3. Cyclic voltammograms of the dispersion coating with different milling duration, (a) 20 hrs, (b) 50 hrs, and (c) 100 hrs at 600 rpm of rotating speed in 1 M HCl solution. Scan rate = 50 mV/s.

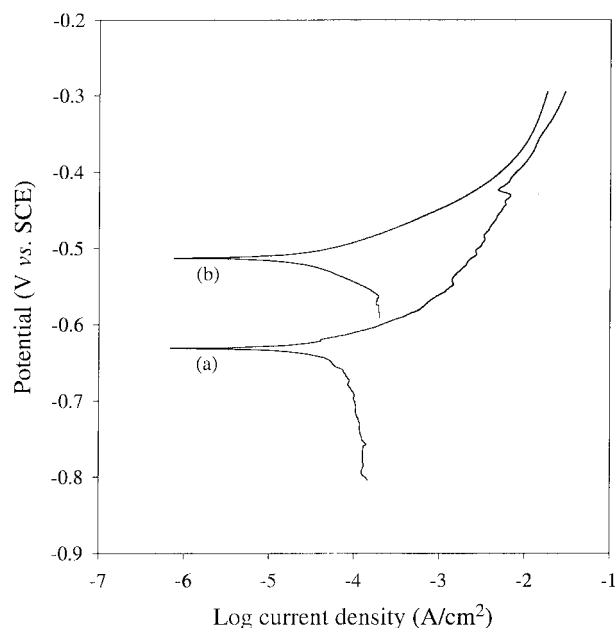


Fig. 4. Potentiodynamic polarization curves of (a) bare steel surface, and (b) PANI dispersion (50 hrs milling at 600 rpm) coating on steel surface in 3 wt.% NaCl solution.

strated inhibiting effect of PANI coating on corrosion of steel surface in neutral salt solution. The steady state values of  $V_{oc}$  of the PANI dispersion coatings on steel surface were recorded around 0.64 V for both of the dispersion coatings, while the  $V_{oc}$  of the bare steel remained at 0.73 V after reaching steady state. This result is also similar to that of Fig 4, and demonstrates protecting ability of the PANI dispersion

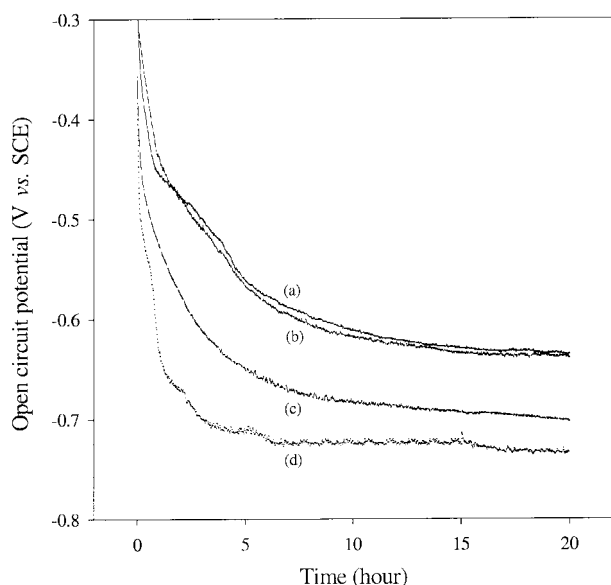


Fig. 5. Open circuit potential ( $V_{oc}$ ) of (a) 70 hr cured PANI dispersion coating (50 hrs milling at 600 rpm) on steel surface, (b) 70 hr cured PANI dispersion coating (100 hrs milling at 600 rpm) on steel surface, (c) 70 hr cured PANI dispersion coating (20 hrs milling at 600 rpm) and (d) bare steel in 3 wt.% NaCl solution.

coating as a practical coating material for corrosion protection of steel. The  $V_{oc}$  of 100 hrs milled dispersion coating was similar to that of 50 hrs milled dispersion coating, while the  $V_{oc}$  of 20 hrs milled dispersion coating is between the 50 hrs milled dispersion coating and bare steel electrode. The  $V_{oc}$  of the other coatings obtained by 60, 70, 80, and 90 hrs milled dispersions also showed the same trend as that of 50 hrs milled coating. It seems that the optimum milling time was achieved at around 50 hrs milling when the rotating speed is 600 rpm, even though the CV curve continually varies with milling duration as shown in Fig. 3. This could also suggest that uniformity and fineness of the particles in the dispersion as well as redox characteristics of PANI coating is the critical factors in determining the capability of the corrosion protective coating.

This work illustrates that the milling conditions such as duration and speed determine the particle size and distribution in the dispersion as shown in Fig. 1, and that variation of milling duration affects redox properties of the PANI coating indicated in Fig. 2. The protective effect of the PANI dispersion coating due to particle size and distribution could be explained by comparison of the  $V_{oc}$  of various PANI dispersion coatings shown in Fig. 5. However, the relationship between redox properties of PANI coating and corrosion protective capability should be further examined through in depth investigation using various PANI materials having different molecular weights. The color change of the coating was observed during  $V_{oc}$  measurements and the detail discussion was presented in elsewhere<sup>23)</sup>.

#### 4. Conclusions

This work shows electrochemistry of PANI dispersion coating and demonstrates practical use of the PANI dispersion made by simple mechanical milling processes as a coating material for corrosion protection of steel. The followings are the summary of the present work.

1. Cyclic voltammetry of the PANI dispersion coating on Pt electrode in 1 M HCl solution showed distinctive redox peaks which is similarly observed in CV of pure polyaniline film, and one small broad redox peak between the two distinctive redox peaks. The broad redox peak is probably due to breakdown of polymer chains during mechanical milling processes.
2. The polarization curve and the open circuit measurements showed that the PANI dispersion coating contributed increased corrosion potential at least 0.1 V toward positive direction.
3. The  $V_{oc}$  measurement indicates that the optimum condition for preparing the PANI dispersion is likely to be achieved at 50 hrs of milling duration with 600 rpm of rotating speed.
4. The color change of the dispersion coating was observed during the polarization experiments and the  $V_{oc}$  measurements. They were discussed in the separate publication.
5. The overall results demonstrate possibility of the practical use of the PANI dispersion made by simple mechanical milling processes to protect steel against corrosion in neutral salt environments.

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