



THE EFFECT OF HYDROGEN DIFFUSIVITIES ON PANI-MODIFIED EPOXY COATING UNDER POTENTIOSTATIC CHARGING

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ABSTRACT

Underground pipelines are susceptible to physical degradation due to the effects of hydrogen permeation which can lead to metallurgical damages, which in turn will affect the service quality. This study employs the use of electrochemical technique to analyze the effects of hydrogen diffusion coefficient on carbon steel coated with Polyaniline (PANI) -modified epoxy in soil solutions at different potentiostatic charging conditions. The protective behavior of PANI-modified epoxy was investigated using adhesion test, hydrogen permeation test and potentiodynamic polarization measurement. The hydrogen diffusion coefficient was determined by the time lag method. The results from these experiments suggest that PANI-modified epoxy is a considerable option for hydrogen barrier coating for steel pipelines in soil environments at certain charging potential.

Keywords: diffusion coefficient, hydrogen permeation, polyaniline (PANI).

INTRODUCTION

Buried pipelines are subject to service degradation resulting from the diffusion of hydrogen (H_2) due to hydrogen evolution reaction which can result in metallurgical damages such as stress corrosion cracking and hydrogen embrittlement. The problem occurs when the hydrogen atom diffuses into the steel. Hydrogen atoms that combine to form H_2 molecules are trapped in the steel, where the gas causes pressure buildup resulting in internal stresses until blisters form near the surface or internal cracks forms deeper within the steel. The hydrogen gas may be caused by corrosion and overprotection conditions of the buried pipelines. This condition is prevalent in buried pipelines which are protected by coating and cathodic protection. However, the failure of coating as the primary protection of the pipelines easily extends the problem to include other factors such as fabrication defect, the presence of bacteria, surface defect, and sour atmospheres to cause the dissimilar current distribution of the cathodic protection and cause pipeline overprotection.

In recent times, Polyniline (PANI) which is one of the conducting polymers has been used as corrosion protection coating [1]–[3]. The research on the ability of PANI as corrosion protection proves that it can provide reliable protection to carbon steel. Inspired by the ability of PANI, we investigated the possible potential of PANI to act as barrier to inhibit hydrogen entry into metal under the influence of potentiostatic charging conditions which are extremely close to real-life situations of transmission buried pipelines. Potentiostatic charging is the technique that uses potentiostate device to force the potential of any metal to a negative region where the metal is stable. This condition is actually similar to the cathodic protection technique which has been applied for many years as secondary corrosion protection after coating. The findings on the success of PANI-modified epoxy as a hydrogen inhibitor led us to investigate further by focusing on the effects of hydrogen diffusion levels on this polymer. Thus,

the electrochemical permeation method was selected because it involves the use of a simple, versatile and competitively priced electrochemical device with high testing sensitivity that gives reliable data. The method was proposed by Devanathan and Starchuski [4] which had been used by other researchers to demonstrate SCC [5], [6], hydrogen embrittlement [7], [8], and common diffusion experiments of several polymers [9]–[11]. In this study, PANI-modified epoxy was used as coating to allow the evaluation of hydrogen diffusion coefficients under different potentiostatic charging conditions. The electrochemical hydrogen permeation method, a mature electrochemical technique, was used to determine the diffusion coefficient of hydrogen. Epoxy was selected as the base of choice for this system as it is one that is widely used as the base for external coating for many physical structures such as pipes, tooling applications, storage tanks, printed circuit boards, reinforcement bars, and most of structural steel.

The rate of hydrogen generation on metal is directly proportionate to the rate of cathodic reaction. This study attempts to observe and explain the influence of cathodic potential on the diffusion behavior and generation of hydrogen on coated steel.

EXPERIMENTAL SECTION

Material and sample preparation

The material used as substrate in this study was API 5L X65 carbon steel with the following composition (weight%): C: 0.07, Si: 0.25, Mn: 1.54, P: 0.013, S: 0.001, Mo: 0.007, Cr: 0.05, Ni: 0.04, Al: 0.041 and balance Fe. As for the hydrogen permeation, the substrate was a 1 mm thick, 2.54 cm² in surface area, disc-shaped piece of metal cut from part of a carbon steel pipeline. Meanwhile, for potentiodynamic polarization measurement, square steel samples with 1.5 cm² surface area was connected to a copper wire and then mounted in hard cold-curing epoxy



resin. After machining, samples were polished, rinsed in distilled water and ethanol. Prior to the application of PANI-modified epoxy coating, the substrate was cleaned by grit blasting to Sa2.5 standard, which can produce typical surface profile of 50-55 μm .

Formulation of PANI-modified epoxy coating

PANI with particle size of 3-100 μm was added to the standard liquid-like diglycidyl ether of bisphenol-A epoxy resin (DGEBA) ($M_w = 380$ g/mol ranging from 0-1.5%). PANI was dissolved in epoxy resin by direct mixing with the addition of toluene as solvent. The solvent was used to render their mutual solubility before curing [12]. However, the solvent was removed once the mixture was soluble. This action was done using a rotary evaporator at the temperature 44 $^{\circ}\text{C}$ and 100 rpm rotation. All chemicals were provided by Sigma Aldrich. The mixtures were added with curing agent (m-xylydiamine) and were stirred for 10 minutes, before application to the steel substrate.

PANI-modified epoxy was applied by brush and dry film thickness was measured using coating thickness gauge, model Elcometer 456. Coating processes were repeated for three times after one week and cured at room temperature to achieve required film thickness. The thickness was set to be in the range below 200 μm .

Adhesion strength measurement

The adhesion strength of the coating on substrate was determined using pull-off technique with adhesion tester, according to ASTM D 4541[13]. The adhesion strength was documented after seven days of curing the samples. The dolly was fixed with the coating's surface using epoxy adhesive (Araldite, Belgium) and was isothermally cured at 80 $^{\circ}\text{C}$ for twenty-four hours in an electric oven. Elcometer model 108 was utilized to pull off the dolly using hydraulic mechanism.

Electrochemical hydrogen permeation test

Hydrogen diffusivities measurements were performed using the electrochemical technique developed by Devanathan and Stachurski [4] and was documented properly in ISO 17081 [14]. A double cell made of polymethyl-methacrylate was employed as shown in Figure-1. The charging solution used to simulate the environmental condition in this study was NS4 solution with the following composition (g/L): 0.122 potassium chloride (KCl), 0.483 sodium bicarbonate (NaHCO_3), 0.181 calcium chloride ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$), and 0.131 magnesium sulfate ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$). NS4 solution is widely used as reference solution to simulate the condition under disbonded pipeline coating [15].

The substrate as working electrode (WE) was held tightly between the two cells by using rubber spacer in such a way that the entire system remained airtight and the solutions on either side of the substrate did not mix. The position of the substrate is as shown in Figure-1. There are two faces of the substrate. The coated side, called the charging side will be facing NS4 solution, while the other side, called the grinded side will be facing the

0.1M NaOH solution. At the charging side the substrate was prepared as mentioned previously. The sample which facing oxidation sides were grounded with 120, 180, 240, 320, and 600 grit silica carbide paper and rinsed with distilled water and followed by ethanol. No palladium coating was applied at the oxidation side. The substrate was sealed by tightening of bolts. A circular area of 2.54 cm^2 was exposed to the solution on both sides. Silver/silver chloride (Ag/AgCl) electrode was used as a reference electrode (RE) and graphite as auxiliary electrode (AE), and both were placed next to the sample in the cell.

First, 0.1 M sodium hydroxide (NaOH) solution was introduced at the oxidation side and was purged with nitrogen gas (N_2) for 1 hour. Then, a constant anodic potential of 300 mV with respect to Ag/AgCl reference electrode was applied. This is a condition where there is almost zero concentration of hydrogen absorption on the oxidation side. The purging gas was maintained at a positive pressure over the solution throughout the entire test period. On the charging side, at which hydrogen gas was to be generated, the potential was maintained at the decided potential. The equipment used for applying required potential was the Autolab Potentiostat/Galvanostat model PGSTAT 128N from Metrohm. The test was carried out at room temperature ($25 \pm 2^{\circ}\text{C}$). The schematic diagram in Figure-1 shows the arrangement of the test.

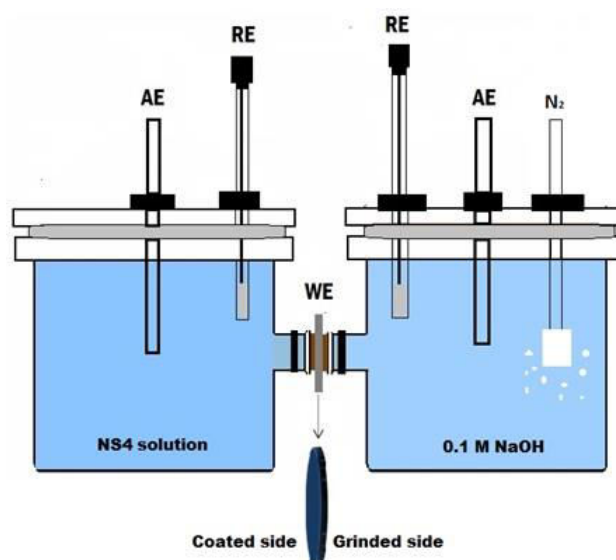


Figure-1. Schematic diagram set-up and sample's position of electrochemical hydrogen permeation test.

Analysis of electrochemical hydrogen permeation test

It is well-known that Devanathan and Stachurski [4] were the first to develop an electrochemical technique based on Fick's first and second law that successfully measured hydrogen diffusivity in alloys. The ASTM G148-97 [16] and ISO 17081-08 [14] was then developed based mostly on the work by Devanathan and Stachurski. The electrochemical technique is a convenient and



accurate method for determining the flux of hydrogen as a function of time [17].

The calculation of hydrogen diffusivity was obtained from the analysis of rising or build-up current in a function of time. Figure-2 shows a typical plot of rising current against experiment times. The hydrogen permeation technique is based on the presumption that well-defined conditions controlling hydrogen entry are established at the charging side of the membrane, so the measured permeation rate of hydrogen is fully controlled by its transporter in the membrane which in this case is carbon steel. However, the delay of current density from zero up to its final steady-state value depends on the insertion reaction kinetics, diffusion behavior and also the sample thickness.

The time-lag method, t_{lag} [16] was used to calculate the hydrogen diffusivity, D in Equation (1):

$$D = \frac{L^2}{6t_{lag}} \quad (1)$$

where the time of t_{lag} is obtained from the time taken for permeation rate to reach 0.63 times the steady state of rising current and L is the thickness of the substrate.

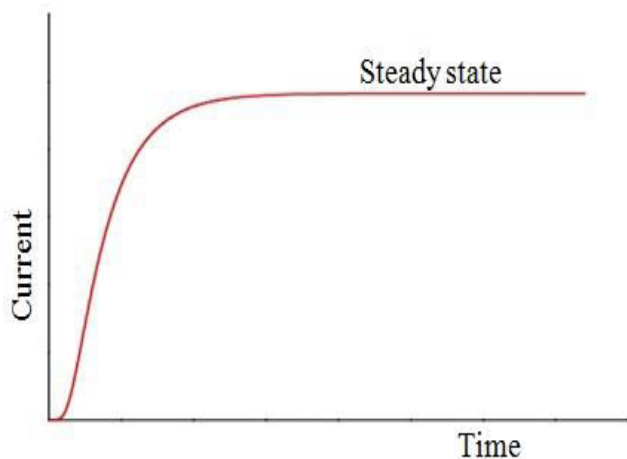


Figure-2. Typical plot for rising current in hydrogen permeation experiment.

Potentiodynamic polarization measurement

Potentiodynamic polarization was done using three-electrode system. The substrate was connected to a copper wire for the purpose of building a connection to potentiostat before it was mounted with clear epoxy resin. The PANI-modified epoxy was applied to the substrate once the epoxy resin has been cured and the blasting process was done on the substrate. A potentiodynamic polarization test was conducted on the substrate in NS4 solution at scan rate 10 mV/min in the range of ± 250 mV_{Ag/AgCl} and were recorded using ACM Gill AC Potentiostat.

RESULT

Adhesion strength of coating

Figure-3 shows the adhesion strength of three types of coated substrate. The adhesion strength showed that epoxy and 1% and 0.5% PANI coating were not much different from each other. Therefore, based on the adhesion test, a 0.5% PANI concentration in epoxy-based system was probably adequate for the coating formulation. The acceptance criteria, shall be a minimum of 7 MPa unless specified otherwise by the end user [13]. Thus, the results revealed that PANI-modified epoxy exhibits an acceptable adhesion property, even with coating that was cured only at room temperature.

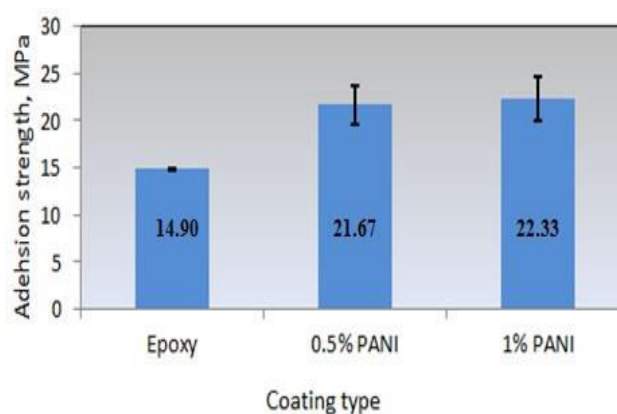


Figure-3. Adhesion strength of coated samples. Hydrogen permeation.

Figure-4 shows the typical hydrogen permeation current as a function of time measured in this work. As expected, after a certain time lag, the hydrogen permeation current increased and then reached a steady state condition. During this period, the effect of hydrogen atom entry into substrate with and without of PANI content in the epoxy was observed. The diffusion coefficient of atomic hydrogen was calculated according to Equation 1. It was noticed that the diffusion coefficient of hydrogen after charging at various potential rates ranged from 10^{-5} to 10^{-7} cm²s⁻¹ as shown in Table-1. Theoretically, the increase of the diffusion coefficient signifies the feasibility to transport the atomic hydrogen within the metal structure. From the data in Table-1, we can assume that current was generated by the hydrogen that was transported through the steel or coating which resulted from the negative potential introduced on the charging side. The investigation at open circuit potential (OCP) was made to simulate the real situation on the field where there is a lack of cathodic protection current or none at all. The diffusion coefficient of hydrogen in the PANI-modified epoxy system determined by using hydrogen permeation technique yielded the lowest rate of diffused hydrogen in 0.5% of PANI concentration.

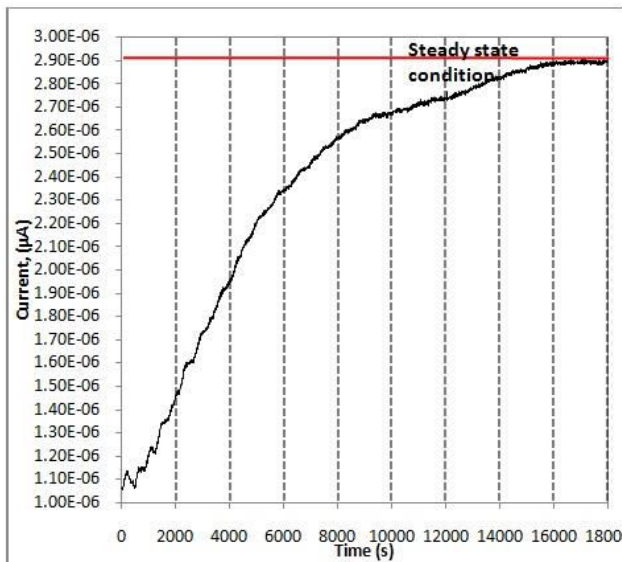


Figure-4. Rising current pattern measured by electrochemical hydrogen permeation on the coated substrate in NS4 solution.

Table-1. The diffusion coefficient of atomic hydrogen measured for the different coating system.

Coating	Diffusion Coefficient, $\text{cm}^2 \text{s}^{-1}$		
	OCP	-900 mV	-1500 mV
Epoxy	9.80E-06	1.38E-07	1.33E-05
0.5% PANI	3.33E-06	4.97E-07	2.47E-07
1.0% PANI	1.45E-05	2.29E-06	1.45E-07
Uncoated	3.17E-07	6.25E-07	6.51E-07

Effect of PANI concentration on Potentiodynamic polarization measurement

Figure-5 compares the polarization curves for the uncoated and coated substrate. The electrochemical data, namely corrosion potential (E_{corr}) and corrosion current density (i_{corr}) were calculated from Figure-5. The results obtained are listed in Table-2. The slope of the tangent at E_{corr} defines the i_{corr} . The i_{corr} was determined by superimposing a straight line along the linear portion of cathodic or anodic curve and extrapolating it through electrode potential [18]. This technique uses data from cathodic or anodic polarization measurements but cathodic polarization data are preferred, since these are easier to measure experimentally [19]. The equation used for calculating the corrosion rate (mm/yr) is as indicated in Equation (2):

$$\text{Corrosion rate, CR (mm/yr)} = K \frac{i_{\text{corr}} \text{EW}}{\rho} \quad (2)$$

Where,

i_{corr} = The corrosion current density ($\mu\text{A}/\text{cm}^2$)

K = A constant that defines the units of the corrosion rate (3.27 mm.g / mA.cm.yr)

EW = Equivalent weight (27.92 g)

ρ = Metal density in (7.86 g/cm³)

In the presence of 0.5% of PANI in the epoxy-based system, the potential of the substrate was shifted towards positive values, but a different situation was observed in 1.0% of PANI concentration in epoxy-based system. The Tafel plot clearly shows the reduction of i_{corr} occurring for the substrate with 0.5% PANI content in epoxy-based system exposed to the NS4 solution.

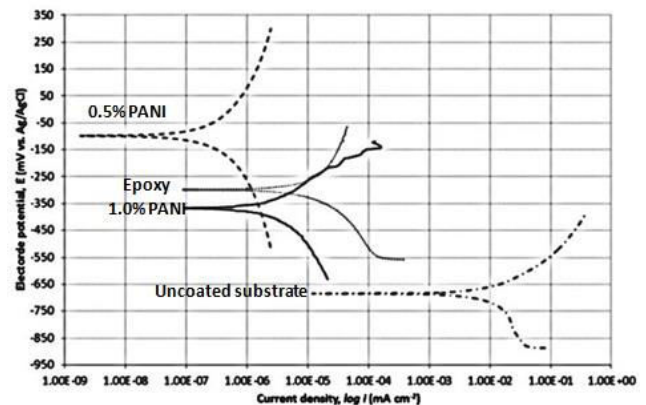


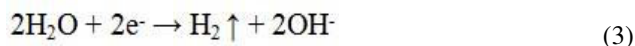
Figure-5. Potentiodynamic polarization plot recorded at scan rate 10 mV/min in NS4 solution.

Table-2. The corrosion rate of coated and uncoated substrate in NS4 solution based on potentiodynamic polarization plot.

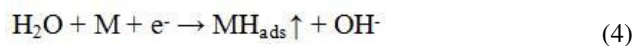
Coating Designation	E_{corr} (mV)	i_{corr} (mA/cm^2)	Corrosion rate (mm/yr)
Epoxy	-298.87	2.31E-05	2.68E-04
0.5% PANI	-102.02	2.03E-04	2.35E-03
1.0% PANI	-367.02	2.52E-02	2.92E-01
Uncoated substrate	-684.15	1.75E-02	2.03E-01

DISCUSSION

For the operation of transmission pipeline in the field, cathodic potential in the range of -850 mV to -1200 mV is usually applied. This is equivalent to about -900 mV, in the carbon steel substrate in NS4 solution at which hydrogen content in the carbon steel reaches peak level [20] which causes service failure of carbon steel pipelines due to problems such as hydrogen embrittlement. At open circuit potential (OCP) no potential was supplied. However, hydrogen was generated due to the dissolution of iron, which produced electrons for the reduction of H^+ . This was confirmed by Y.F. Cheng *et al.* [6] in their work. They successfully demonstrated the hydrogen evolution kinetics which was significant, with a hydrogen evolution process at open circuit potential. Under potentiostatic charging condition, the potential was applied to the substrate, thus dissolution of carbon steel was prohibited. Hydrogen reduction takes place during water decomposition in NS4 solution via the following reactions [21];



H^+ was reduced by the cathodic current at the charging side and the OH^- diffused to the oxidation site in the oxidation process. These reactions take place in two steps where M is surface metal atom.



The adsorbed hydrogen atoms (H_{ads}) can combine with each other to form molecular hydrogen and are released from the electrolyte as gas bubbles or they can diffuse into the material as absorbed hydrogen (H_{abs}).



In comparison with uncoated substrate, the presence of PANI-modified epoxy can promote the reduction reaction of H atoms and retard the dissolution of Fe. This was concluded based on the reduction of corrosion rate and diffusion coefficient of the sample in the presence of PANI as an external coating in epoxy-based system in NS4 solution. The reduction of hydrogen atom diffusion in coated substrate, especially in the presence of PANI, is the result of the lesser hydrogen production on the charging side. The difference of hydrogen diffusion levels in the steel is probably due to some process in higher concentration PANI that block the hydrogen/hydroxide pathway. The reliability of the permeation data depends greatly upon the stability of the coating layer on the charging side of the substrate [22]. The above result in Table-1 proves that the diffusion coefficient of hydrogen value was affected by the application of cathodic potential on surface processes at the charging side. The diffusion coefficient was lower in magnitude after charging with more negative potential for substrate coated without PANI at certain amount of concentration.

The electrochemical reaction that occurs at the steel-electrolyte interface increased the adsorbed hydrogen prior to the formation of atomic or molecular hydrogen. The hydrogen bubble on the substrate at the charging side was clearly observed, especially at -1500 mV of charging potential to all substrate but the number of bubbles declined for coated substrate. On the grinded side, the reduction of hydrogen adsorption was obtained in the presence of epoxy for substrate charging at -900 mV which is $1.38 \times 10^{-7} \text{ cm}^2 \cdot \text{s}^{-1}$ but it was higher at high potential charging condition (-1500 mV) with $1.33 \times 10^{-5} \text{ cm}^2 \cdot \text{s}^{-1}$. On the other hand, in the presence of 1.0 % PANI with high charging potential (-1500mV) where the value of diffusion coefficient is $1.45 \times 10^{-7} \text{ cm}^2 \cdot \text{s}^{-1}$, better reduction of hydrogen adsorption was observed.

The influence of potentiostatic charging on the hydrogen concentration of the substrate can be correlated to the behavior of coatings containing different concentration of PANI in epoxy-based system. C. Dong, A.Fu, And X.Li [23] showed in their work, with the decreasing rate of cathodic potential, the diffusive

impedance and charge-transfer resistance will also decrease. As a result, loss of adhesion between coating and steel occurred. Good performance of the coating during service is one of the major important issues. In this study, the adhesion of coating fall within the range of 14.9 to 21.3 MPa. The adhesive strength was quite high for all coating systems. It is because epoxy paint is well known for high adhesive strength due to the presence of polar groups in the structure [24]. When epoxy contains PANI, PANI works as the system of barrier as it participates in hydrogen bonding and other polar interactions with epoxy resin [24]. In this study, 1.0% of PANI content in epoxy has the highest adhesive strength among all coating systems.

A similar discussion can be carried out in the observation of potentiodynamic polarization curve for coated and uncoated sample. Interestingly, the result from [12], [25] and ours shows very clear evidence of the reduction of i_{corr} from polarization curve. They also successfully show the significant corrosion protection provided to steel in the presence of PANI compared to substrate coated with epoxy alone. Furthermore, the measurement of potentiodynamic polarization measurement indicated that the presence of PANI in epoxy-based system alters the electrochemical corrosion processes occurring on the substrate [6]. Again, the corrosion rate of coated substrate variation was clearly observed in this study. The lowest corrosion rate observed was for substrate coated by epoxy alone which is $2.68 \times 10^{-4} \text{ mm/yr}$, even though the highest E_{corr} was observed for substrate coated by 0.5% PANI-modified epoxy. The above results indicate that epoxy alone was good enough to protect metal substrate in terms of external corrosion in alkaline environment. This was proven by the lower corrosion rate observed of the uncoated substrate, which is $2.03 \times 10^{-1} \text{ mm/yr}$. In addition, lower concentration of PANI in epoxy-based system protected metal substrate better than coating with higher concentration of PANI content, when exposed in alkaline solutions. We believe that the main protection mechanism of PANI through the formation of a protective metal oxide layer, which is thought to passivate the metal surface is more practical in acidic and neutral media rather than in alkaline media. S. Sathiyarayanan *et al.* [26] showed that the PANI-pigmented coatings were highly protective in acidic compared to neutral media. It also passivates the iron surface and enhances its protective property. However, the corrosion protection on metal still depends on the PANI properties and the nature of the corrosion environment.

CONCLUSIONS

In summary, the hydrogen permeation test data agreed that the performance of coating in epoxy-based systems with certain potential charging environments improved with the addition of PANI at certain concentration. The results from this study at the moment shows that under higher potentiostatic charging condition, the 1.0% PANI-modified epoxy has appreciable ability in reducing hydrogen permeation, but the lowest corrosion



protection ability compared to other coating systems used in this study. Furthermore, the adhesion strength test showed that epoxy alone on substrate was a fairly good protection mechanism. Further evidence to support this is obtained from the potentiodynamic polarization plot by calculating the corrosion rate from i_{corr} . The above results have shown that the addition of PANI in epoxy-based system has the ability to reduce the hydrogen diffusivity in alkaline media such as NS4 solution depending on the cathodic charging potential. However, further study should be done in a variety of corrosive environments, especially at different pH levels before a concrete conclusion can be made.

ACKNOWLEDGEMENTS

The authors would like to acknowledge the Universiti Teknologi PETRONAS, (UTP) and Centre for Corrosion Research, (CCR). This work was funded by the Malaysian government MyBrain program.

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