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TECHNOLOGYEVALUATE PERFORMANCE AND ANALYSIS CORROSION PRODUCTS FOR
CARBON STEEL IN ACIDIC MEDIA

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ABSTRACT

The performance of carbon steel (C1010) has been evaluated in three acidic solutions: 1M HCL, 1M H₂SO₄, 1M CH₃COOH after immersion for 30 minutes and 300 minutes. The corrosion rate was determined by linear polarization resistance and potentiodynamic polarization techniques, and the corrosion rate in a short time of immersion was slightly higher than in a longer period of immersion due to deposits of the corrosion product on the sample surface slowing down the cathodic reaction rate and metal dissolution (anodic reaction), which can be clearly seen in PDP curves. In addition, X-ray photoelectron spectra was used to provide information on the actual compound present on the sample surface. Fe 2p, O 1s, Cl 2p, S 2p, C 1s core level spectra demonstrate that substrate termination does vary according to acidic solution type, with chloridic, sulfate, and acetate films being exhibited on top of the surfaces of samples when immersed in 1M HCl, 1M CH₃COOH, and 1M H₂SO₄ respectively. The information provided by XPS supports and complements the data obtained from other techniques as mentioned above. All results indicate that the corrosion resistance of carbon steel in acetic acid is higher than hydrochloric acid or sulfuric acid due to the higher rate of hydrogen evolution in the latter. In other words, the worsening of surface film stability in carbon steel occurs much faster in H₂SO₄ than HCl or CH₃COOH.

KEYWORDS: Carbon steel (C1010), 1M HCL, 1M H₂SO₄, 1M CH₃COOH, PDP, XPS.

INTRODUCTION

Carbon steel is widely utilized in many engineering applications and industrial environments due to cheaper and has a good mechanical properties[1]. Acidic media especially hydrochloric acid and sulfite acid is used in many industrial processes like pickling in order to remove undesirable scale and rust which leads corrosion on the iron materials, therefore studying behaviour corrosion for carbon steel in different acidic condition is very important to find out which is suitable method to prevent or reduction corrosion rate[2]. In real practice, most acidic industrial applications such as crude oil refining among other processes in oil recovery and processes in petrochemicals tend to utilize carbon steel as a material. According to Matthew (2008), as acidic media, acetic acid (CH₃COOH), sulfuric acids (H₂SO₄) and hydrochloric acids (HCl) are used in industrial cleaners as well as pickling acids. In this case, large numbers of organic elements indicate that nitrogen, sulphur and oxygen contain organic elements that act as promising inhibitors. Nevertheless, most compounds are expensive and toxic to living things.

According to the reference [3] the corrosion reaction chemistry in acid corrosion, considering iron in dilute hydrochloric acid solution as shown in equation below:



where the subscribe m, l, and g indicate the phases solid metal, liquid aqueous solution and gas, containing the species solid pure iron, dissolved hydrochloric acid, dissolved ferrous chloride, and gas hydrogen, respectively. In this particular case the situation is simple hydrogen chloride and ferrous chloride are strong electrolytes, virtually completely dissociated into dissolved ions H⁺, Cl⁻, and Fe²⁺[10].

Instead of hydrochloric acid, sulfuric acid can be considered just as well, and the reaction equation then is



Arbitrary assuming complete dissociation of H₂SO₄ into H⁺ and SO₄²⁻, while in case acetic acid the reaction equation then is



The research will focus on an evaluation of performance of carbon steel in all acidic solutions and in this case, three acidic solutions. It will also study all actual compounds that are available on the surface through application of X-ray photoelectron spectroscopy technique.

EXPERIMENTAL PROCEDURE

The experimental procedure is to determine the corrosion of carbon steel and provide substrate termination present on the top of the surface when immersed in three acidic conditions as mention above. The linear polarization resistance (LPR) and potential dynamic polarization (PDP) were taken after 30 minutes and 300 minutes of immersion in stagnant 1000 mL solution while the XPS technique was taken after 30 and 300 minutes of immersion in 50 mL of solution.

Sample preparation for electrochemical measurement and Instrument set up:

Square carbon steel (C1010) samples were cut from the coupon with dimensions of 1 cm x 1 cm. Carbon steel has a composition %C (0.08-0.13), %Mn (0.3-0.6), %P 0.04, %S 0.05, and remaining %Fe. In order to feed the electrical connection with the potentiostat, the samples were welded to the copper wire. The plastic tube covered the copper wire to protect it from corrosion. The sample was put into resin. The specimens were mechanically polished using sand paper (silicon carbide) starting from 120 up to 800. The surface of the sample was degreased with ethanol and deionized water, and then dried by flow air.

As shown in Figure (1), The electrochemical measuring was tested in a cell and was contained from three electrodes. The sample or working electrode was completely immersed in solution. The platinum electrode was used as an auxiliary electrode, while the reference electrode was utilized from Standard Calomel Electrode (SCE). The three electrodes were put inside a beaker. The beaker was covered as shown in Figure (1).

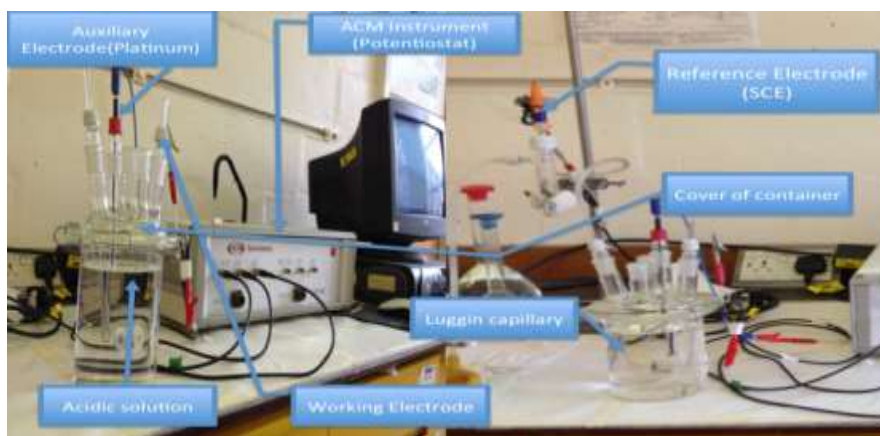


Figure (1) Electrochemical measuring cell and luggin capillary

A potentiostat from ACM instruments managed by computer was connected to the cell as shown in Figure (1). Both LPR and PDP were utilized in this test. The LPR technique was applied in the potential sweep range ± 10 mV from open circuit potential (OCP) with sweep rate 10mV/Min. The LPR was measured every 15 minutes up to 300 minutes, and following that ,the PDP technique was achieved in the potential sweep rate ± 250 mV with a sweep rate of 60 mV/Min. The latter test was repeated for a second time after 30 minutes of immersion.

Sample preparation for XPS technique and Instrument set up:

Small coupons were made from carbon steel (C1010) with dimensions of 1 cm x 1.5 cm. Both surfaces and sides were mechanically polished using silicone carbide paper starting from 600 up to 4000. Following the change of each paper, the sample was washed by deionized water and ethanol, and then dried by flow air to avoid any contamination and atmospheric corrosion. After that, it was finished with diamond polishing up to one micron with a solution. All samples were cleaned by an ultrasonic cleaning bath with acetone for ten minutes and then rinsed with ethanol and deionized water and then dried by flow air.

Eight samples were prepared in the XPS study by using the procedure as mentioned in above. Three of the samples were immersed in solutions 1M HCL, 1M H₂SO₄, 1M CH₃COOH for 300 minutes and the other three samples were immersed in the same solutions for 30 minutes which were immersed after the last 30 minutes from the test into the glove box with nitrogen purge as shown in Figure (2-A). The seventh sample was left polished, only without immersion in solution for the base case while the eighth sample was immersed in solution containing 1 M HCL with inhibitor 2mM MBI which was used to check if there was oxygen ingress or not from previous work[5]. All specimens were suspended by Teflon wire into beakers containing 50 mL of solution. The nitrogen purge was used to dry the samples and they were put directly on the sample bar utilizing double sided adhesive tape as shown in Figure (2-B). High vacuum conditions were used in the XPS technique to avoid the effect of O₂ on the surface layer.

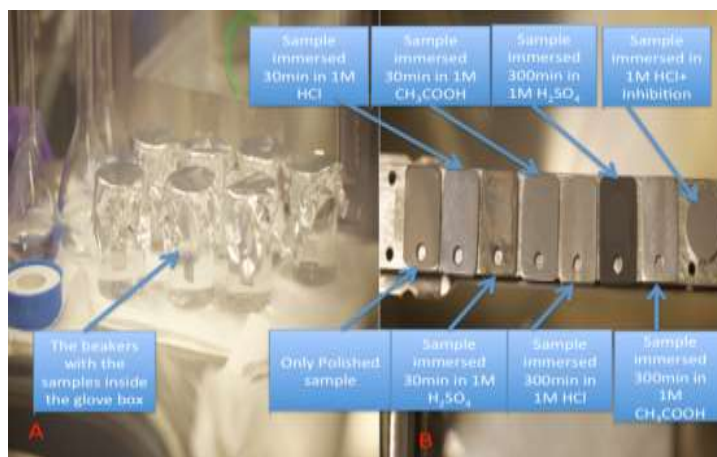


Figure (2) Samples inside the glove box, A) Inside of beaker before being taken out, B) on the sample bar after being taken out of solution

The X-Ray photoelectron spectroscopy was achieved in a Kratos Axis Ultra instrument utilizing Monochromated Al K α X-ray ($h\nu$ 1486.6 eV, $\Delta h \approx 0.6$ eV) as the photon source. The emitted photoelectrons were picked up via a hemispherical (165 mm) energy analyzer mixing a delay line detection system. The focus area was analyzed $\sim 0.7\text{mm} \times 0.3\text{mm}$. The energy of 80 eV was passed for wide energy scan, overview spectra analyzer. The energy of 20 eV was passed for high energy resolution spectra of single core levels. Throughout the measurements, both 0° and 50° photoelectron emission angles were used [4].

RESULTS AND DISCUSSION

From electrochemical results, Table (1) illustrates the corrosion rate which was determined by Linear Polarization resistance (LPR) after 30 minutes and 300 minutes of immersion in 1M HCL, 1M H₂SO₄, 1M CH₃COOH. As expected, the corrosion rate was higher in sulfuric acid and hydrochloric acid, while it was lower in acetic acid in both immersion times of 30 and 300 minutes.

It should be noted that in order to determine corrosion rates of sulfuric and hydrochloric acids from the LPR data, $B = 26$ mV (Stern-Geary coefficient) was employed for samples exhibiting activation controlled corrosion kinetics as discerned from PDP data; this value is consistent with the anodic/cathodic Tafel constants corresponding PDP curves as shown in Figures (3) and (4). $B = 52$ mV was used to determine corrosion rates for samples immersed in acetic acid, displaying diffusion controlled kinetics[6,9].

Also, it can be seen from Table (1) that the corrosion rate after 30 minutes of immersion was slightly higher than the corrosion rate after 300 minutes because the corrosion product which covered the surface retarded the corrosion of carbon steel, but did not completely stop the corrosion process which means that the corrosion film product is not adherent or compact enough to protect material from further corrosion. This hypothesis is supported by the visual

inspection in which it was noticed that the reaction rate for hydrogen evolution was slowed down during the immersion over time. Figures (3) and (4) illustrate the potentiodynamic polarisation curves after the immersion of carbon steel for 30 minutes and 300 minutes in 1M HCL, 1M H₂SO₄, 1MCH₃COOH respectively. From PDP curves, it can be seen that the open circuit potential (OCP) was less negative in samples treated with sulfuric acid than hydrochloric acid or acetic acid which means that the rate of HER was highest in sulfuric acid, and that led to an increase in the cathodic current limited and at the same time led to metal dissolving which means that increasing the rate of anodic reaction. On the other hand, it can be noted that the current density for samples treated with acetic acid was much lower than HCl or H₂SO₄. From PDP plots, it can be noticed that at higher current density away from corrosion potential there is a curvature in both anodic and cathodic reactions due to IR drop in solutions[9]. In addition, another factor was observed that led to increasing the current density for cathodic reaction for samples immersed in sulfuric acid which is due to the higher rate of hydrogen evolution lead to support the cathodic limited current which means more dissolved of metal ion (anodic reaction) to conclude from that the PDP curves are supported the corrosion rate as shown in Table (1).

Table 1. Corrosion rate in three acidic solutions for 30 min and 300 min

Time of Immersion	1M HCL	1M H ₂ SO ₄	1M CH ₃ COOH
30 Minutes	5.9 mm/Year	20.7 mm/Year	0.91 mm/Year
300 Minutes	4.8 mm/Year	19 mm/Year	0.83 mm/Year

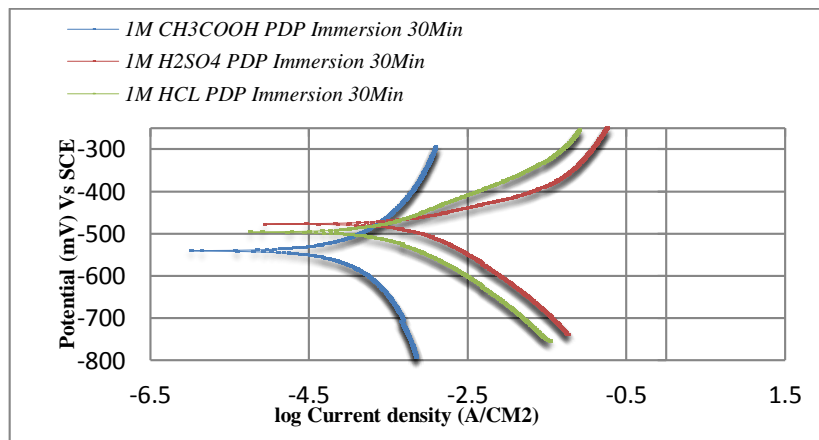


Figure (3) Carbon Steel Immersion in three acidic solutions for 30min

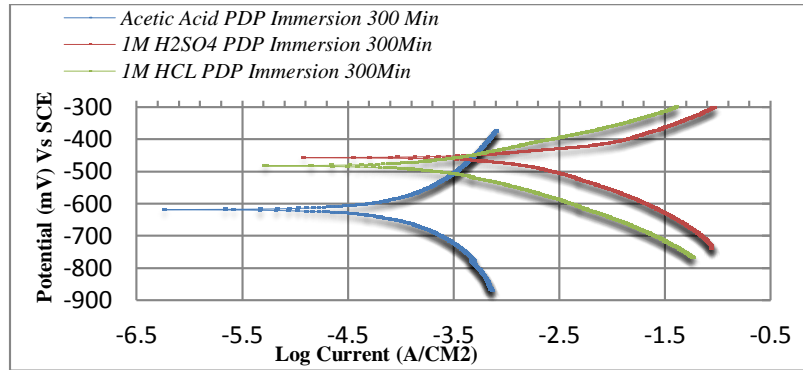


Figure (4) Carbon Steel Immersion in three acidic solutions for 300min

XPS Results and Discussion

The Overview XPS

The Overview XPS spectra ($\theta_E = 0^\circ$) of carbon steel specimens after 30 min and 300 min of immersion in 1M HCL, 1M CH_3COOH , 1M H_2SO_4 and one polished specimen (as a reference used to compare our data) were observed in Figure (5). The CasaXPS software was utilized to label referenced??? to the standard binding energy, which are expected elements Fe, O, Cl, S, and C. The binding energy value of 285 eV to the C 1s hydrocarbon component of adsorbed adventitious carbon was assigned to calibrate all binding energy scales [4].

Generally, from Figure (5), in the case of samples only polished, three peaks were observed which consisted of Fe 2p acquires from carbon steel substrate, O 1s arising from an oxide surface film deposit on top of the surface plus adsorbed species and C 1s which is contamination from air, while in samples exposed to hydrochloric acid, Cl 2p peak as (a normal arising from chloride ions) with three peaks was observed, as mentioned above. Sulfur peak was found when samples were immersed in sulfuric acid solution, whereas the carbon peak slightly increases when samples are immersed in acetic acid solution.

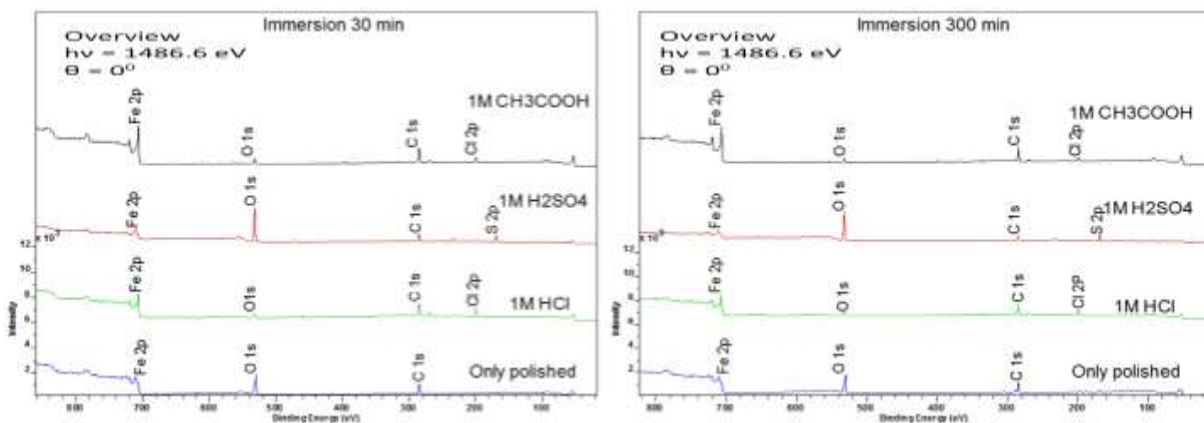


Figure (5) Overview XPS spectra acquired from carbon steel specimens exposed to the following treatments for (30 min left and 300 right); polished only; immersed in 1M HCl solution; immersed in 1M CH_3COOH solution; immersed in 1M H_2SO_4

Higher resolution XPS

From figure (6), it can be noticed that the peak for substrate Fe^0 and mixed of Fe^{2+}/Fe^{3+} varied in the case of the polished sample, and after samples were immersed in acidic solutions. From previous work [4], in the case of the polished sample, the Fe^0 intensity arose from the clear metal surface while Fe^{2+}/Fe^{3+} signal arose from the metal oxide because the surface was exposed to the air. Also it can be noticed that after the specimen was immersed in 1M HCl, the signal of Fe^0 significantly increased, whereas the signal of Fe^{2+}/Fe^{3+} slightly decreased as a result of replacing iron oxide with iron chloride. After the sample was immersed in 1M CH_3COOH , the signal of Fe^0 sharply increased while the signal of Fe^{2+}/Fe^{3+} significantly decreased due to replacing iron oxide with iron acetate. When the sample was immersed in 1M H_2SO_4 , it was observed that the signal of Fe^0 sharply decreased while the signal of Fe^{2+}/Fe^{3+} significantly increased due to replacing iron oxide with iron sulfate which means that this information supports the results as shown in table (1) by using electrochemical measurement.

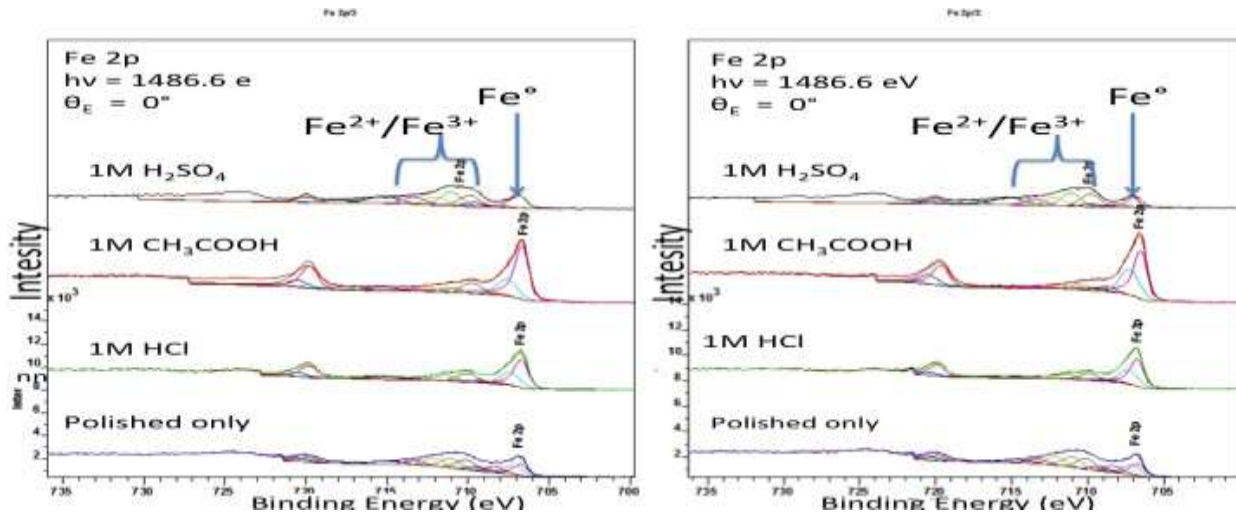


Figure (6) Energy spectrum for iron ion on surface of carbon steel immersed in acidic solution (left) immersion 30min, (Right) immersion 300min.

From Figure (7), (Energy spectrum for higher resolution of oxygen), it can be noticed that the polished Fe sample revealed the 2 lower O 1s binding energy which are labeled O^{2-} , OH^- (led to form iron oxide/hydroxide as a normal oxidic film when the sample exposed to the moisture air) and 2 higher binding energy labeled as (O^1 and O^2) as well. Also of significance is the disappearance of O^{2-} and OH^- when the samples were immersed in acidic solutions due to the oxidic film being dissolved in these solutions and being replaced with iron chloride, iron acetate and iron sulfate when the samples were immersed in 1M HCl, 1M CH_3COOH , 1M H_2SO_4 respectively [4].

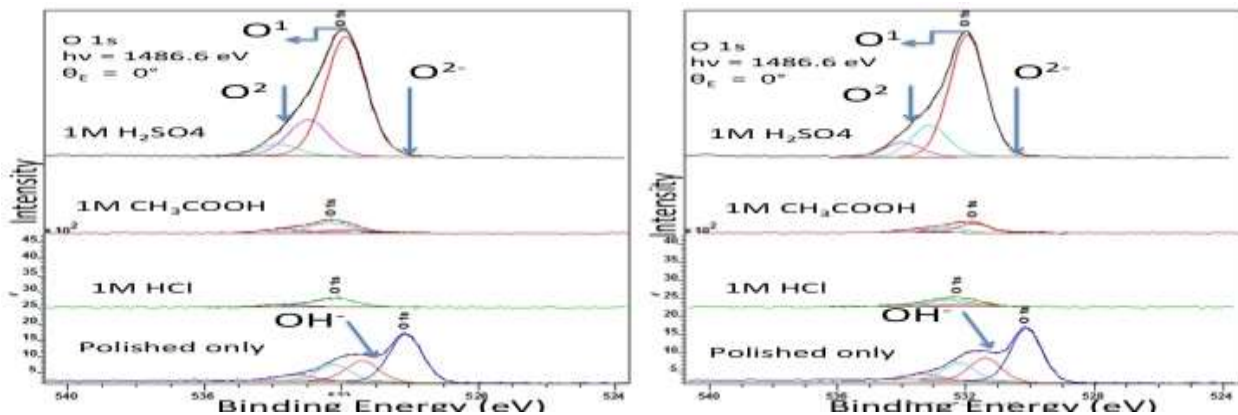


Figure (7) Energy spectrum for Oxygen ion on surface of carbon steel immersed in acidic solutions (left) immersion 30min, (Right) immersion 300min.

Furthermore, the peak intensity (O1s) when the sample was immersed in sulfuric acid is higher than in hydrochloric acid or acetic acid, resulting in an increase in the corrosion rate due to the presence of sulfate ions will lead to dissolve iron metal (anodic reaction) throughout provide more hydrogen evolution (cathodic reaction). This is good evidence to support electrochemical measurements as shown in table (5-1), which recorded the higher corrosion rate when the carbon steel was immersed in sulfuric acid.

From Figure (8), (energy spectrum for higher resolution of sulfur signal), it can be seen that no sulfur signal was found in the polished sample or in the samples treated with hydrochloric acid or acetic acid. A signal of sulfur was only found in the sample treated with sulfuric acid which was a normal source to provide the sulfur which was compounded with oxygen to form sulfate and sulfuric acid is more corrosive than hydrochloric acid. This is in agreement with previous work [7], which found the corrosion rate to be higher for samples treated with H₂SO₄ than hydrochloric acid.

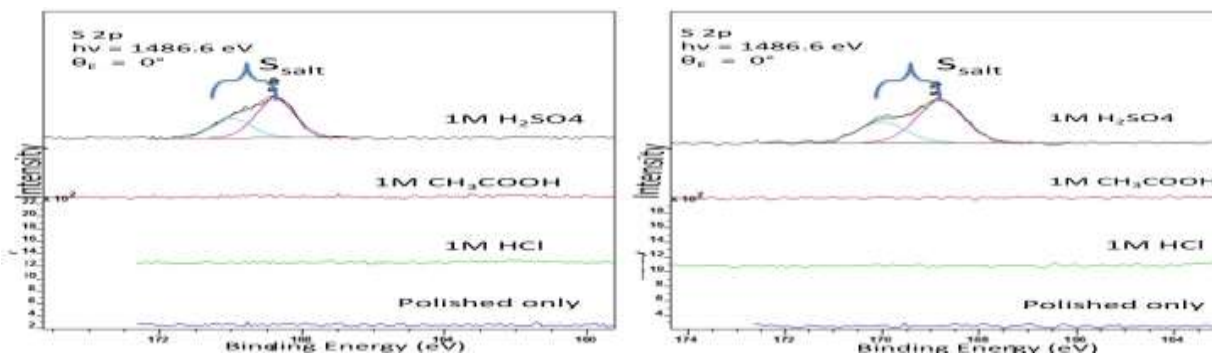


Figure (8) Energy spectrum for sulfur ion on surface of carbon steel immersed in acid solution (Left) immersion 30min, (Right) immersion 300min.

From Figure (9) (energy spectrum for higher resolution of chloride signal), it can be seen that no chloride signal was observed in the polished sample or in the samples treated with sulfuric acid, which is an expected observation, while in samples treated with hydrochloric acid the signal of chloride was clearly noticed which was bonded with iron ions as mentioned above to form iron chloride instead of iron oxide or hydroxide, and chloride ion is corrosive, leading to an increase in the corrosion rate. Also, it can be seen that there is a signal found in samples treated with acetic acid which was unusual to see, and it definitely came from contamination during the preparation of the samples or the solution in which the samples were immersed[8].

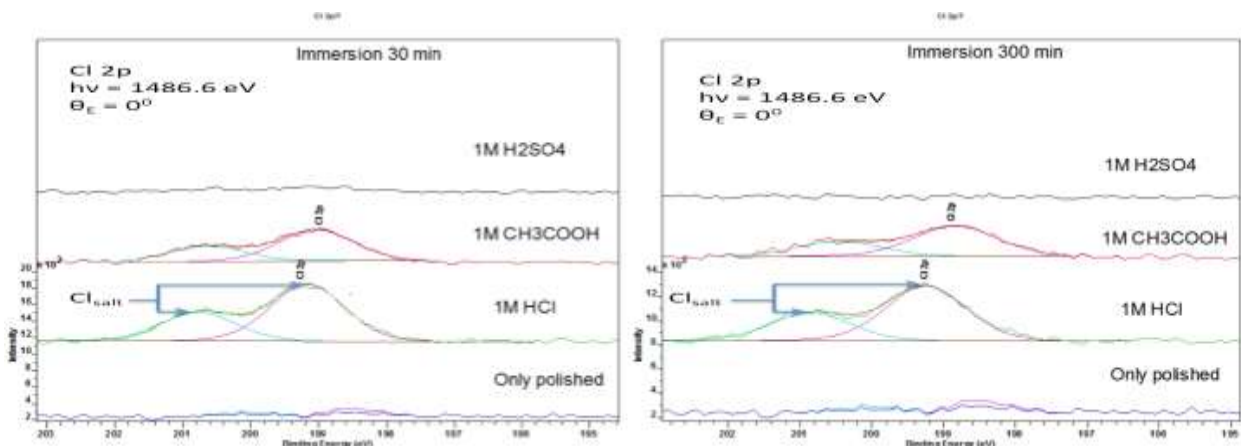


Figure (9) Energy spectrum for chloride ion on surface of carbon steel immersed in acidic solutions, (Left) immersion 30min, (Right) 300min.

From Figure (10), (energy spectrum for higher resolution of carbon signal), it can be seen that in all samples treated with acidic solution, including polished samples, a signal of carbon was observed which seemed to be of a similar

intensity, except the sample which was treated with acetic acid which had a slightly higher intensity, possibly due to an extra carbon atom in composition of acetic acid. However, this is not strong evidence to prove this hypothesis. There was a low corrosion rate in the samples treated with acetic acid when compared with sulfate ion or chloride ion due to form iron acetate, which was less corrosive than iron sulfate or iron chloride[8].

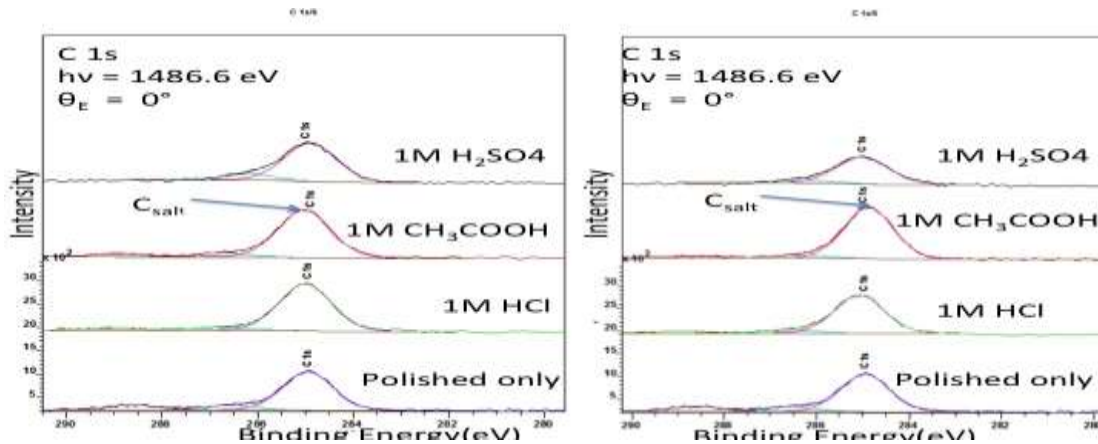


Figure (10) Energy spectrum for carbon ion deposit on surface of carbon steel immersed in acidic solutions, (Left) immersion 30min, (Right) immersion 300min.

CONCLUSION

Overall, it is concluded that the highest corrosion rate was recorded with sulfuric acid, while the lowest was recorded with acetic acid and hydrochloric acid. LPR data proves that the corrosion resistance for carbon steel in acetic acid is higher than in sulfuric acid or hydrochloric acid which means, in other words, carbon steel surfaces will be more damaged with H_2SO_4 or HCl. PDP plots indicate that the current density for cathodic reaction increases with an increase in hydrogen evolution, leading to the dissolution of metal (anodic reaction). As a result, PDP curves is supported by the LPR data. XPS depth profiles show the binding energy of Fe, C, O, Cl elements in corrosion film when immersed in HCL solution and Fe, C, O, S elements in case immersion in sulfuric acid, while Fe, C, O elements were samples treated with acetic acid. Fe 2p, O 1s, Cl 2p, S 2p, C 1s core level spectra demonstrate that substrate termination does vary according to acidic solution type, with chloridic, sulfate, and acetate films being exhibited on top of the surface of samples when immersed in 1M HCl, 1M H_2SO_4 and 1M CH_3COOH . From higher resolution spectra, it can be seen that the intensity for substrate (Fe^0) was lower in samples treated with sulfuric acid than hydrochloric acid or acetic acid, indicating that the surface layer forming is getting thicker due to the rate of hydrogen production being higher with sulfuric acid lead to support cathodic current limit and dissolve more metal ions (anodic current) which means that is much more aggressive than acetic acid or more aggressive than hydrochloric acid. As revealed by the present results in this project, the deterioration of surface film stability occurs much faster in H_2SO_4 than HCl or CH_3COOH because the rate of hydrogen production is higher with sulfuric acid which is more corrosive than chloridic or acetate, causing more damage to the surface.

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