

## Development of Iridium Oxide Sensor for Surface pH Measurement of a Corroding Metal under Deposit

Jalal Rouhi<sup>1</sup>, Saeid Kakooei<sup>2,\*</sup>, Mokhtar Che Ismail<sup>2</sup>, Rouhollah Karimzadeh<sup>1</sup>,  
Mohamad Rusop Mahmood<sup>3</sup>

<sup>1</sup> Department of Physics, Shahid Beheshti University, Evin, Tehran 19839, Iran

<sup>2</sup> Centre for Corrosion Research, Department of Mechanical Engineering, Universiti Teknologi PETRONAS, Tronoh31750, Malaysia

<sup>3</sup> Centre of Nanoscience and Nanotechnology (NANO-SciTech Centre), Institute of Science, Universiti Teknologi MARA, Shah Alam, Selangor 40450, Malaysia

\*E-mail: [skakooei59@hotmail.com](mailto:skakooei59@hotmail.com), [saeid.kakooei@utp.edu.my](mailto:saeid.kakooei@utp.edu.my)

Received: 29 May 2017 / Accepted: 21 August 2017 / Published: 12 October 2017

---

A novel method used to design and fabricate a pH sensor for measurement of hydrogen ion activity on corroding metal surface in under deposit. The electrodeposition method of cyclic voltammetry approach is used for coating of Iridium Oxide ( $\text{IrO}_x$ ) on stainless steel substrate. The pH value of the X52 carbon steel under deposit (agar) was monitored for the first time using the in-situ iridium oxide pH probe during the  $\text{CO}_2$  corrosion at 25 and 80°C. Cyclic voltammetry (CV), field emission scanning electron microscopy (FESEM), energy-dispersive X-ray spectroscopy (EDX), Linear polarization resistance (LPR), and open circuit potential (OCP) were used for  $\text{CO}_2$  corrosion and iridium oxide film characterization. The fabricated pH sensor was calibrated by using a commercial glass pH probe. The response of electrodeposited  $\text{IrO}_x$  electrodes to exposure to a series of universal buffer solutions depicts a linear super-Nernstian response resulting in a sensitivity of  $-77.18$  mV/pH for combination of three  $\text{IrO}_x$  pH sensors. The pH response measured by OCP at 25 °C was 75.3 mV/pH units. The pH of metal surface under deposit increased gradually up to pH=8 after exposure in  $\text{CO}_2$ -saturated 3% NaCl solution compared to the bulk solution pH (pH=6). Results demonstrated the proposed pH sensor design can be used for real-time corrosion monitoring by surface pH measurement. The design approves that the measurement was able to determine the pH changes under agar, which is a critical requirement for studying corrosion under deposit. In all cases, metal surface pH under deposit increased compared with bulk solution pH after the corrosion process began. These findings indicate that  $\text{IrO}_x$  pH sensor material can be changed to any other sensing material which is very useful for monitoring of MIC or other kind of corrosion.

---

**Keywords:**  $\text{IrO}_x$  pH sensor; Electrodeposition method; Surface pH measurement; Cyclic voltammetry

## 1. INTRODUCTION

Recently, Iridium oxide (IrO<sub>x</sub>) became a superior material for reference electrode [1], food-industry [2], nuclear field [3], and pH measurements in various fields such as biological media [4]. Various solid-state metal oxides have been investigated for pH sensing electrodes. Typically, the pH sensitivity, selectivity, working range, and hysteresis indicate sensing performance. IrO<sub>x</sub>, RuO<sub>2</sub> and SnO<sub>2</sub> have been demonstrated with more advantages in sensor performance for various applications compared to others [5].

In 1996, Roe et al. measured dissolved oxygen, pH, and ion currents on steel corroded surface using three closely spaced microelectrodes [6]. They proposed a real time mapping of the pH distribution on the steel corroded surface. Since biocompatibility and corrosion resistance of IrO<sub>x</sub> electrodes are noticeable; these electrodes can be as a potential candidate for microbial induced corrosion investigation [7]. Iridium oxide film has performed outstanding stability over wide pH range, rapid responses, less potential drift and high durability, which have also been tested at high temperature up to 250 °C [8].

It is clear that preparation methods play the main role in the pH response of the iridium oxide-based electrodes. Anhydrous iridium oxides were achieved by thermal oxidation or sputtering methods, which showed a pH response of 59 mV/pH, whereas iridium oxides fabricated by electrochemical technique are predominantly hydrated iridium oxides such as IrO<sub>2</sub>•4H<sub>2</sub>O, Ir(OH)<sub>4</sub>•2H<sub>2</sub>O, which present a super-Nernstian response 90 mV/pH unit [9].

Under deposit corrosion is one of significant reason for main damage of boiler tubes, oil and gas pipelines [10], oil and gas production systems [11]. Lack of proper facility for doing pH measurement under deposit is commonly highlighted. A proper design of experiment is necessary to be designed for surface pH measurement of a corroding metal under deposit.

Nyborg et al. investigated under deposit corrosion by developing a new test method [12]. They used three carbon steel working electrode in conjunction with a reference electrode which were mounted together in an assembly. Sand was used as deposit to cover two of the specimens. The galvanic current and potential difference between sand covered and not covered specimens were determined. They measured the corrosion rate of all three specimens by LPR measurements, while the galvanic current is measured by zero resistance ammetry.

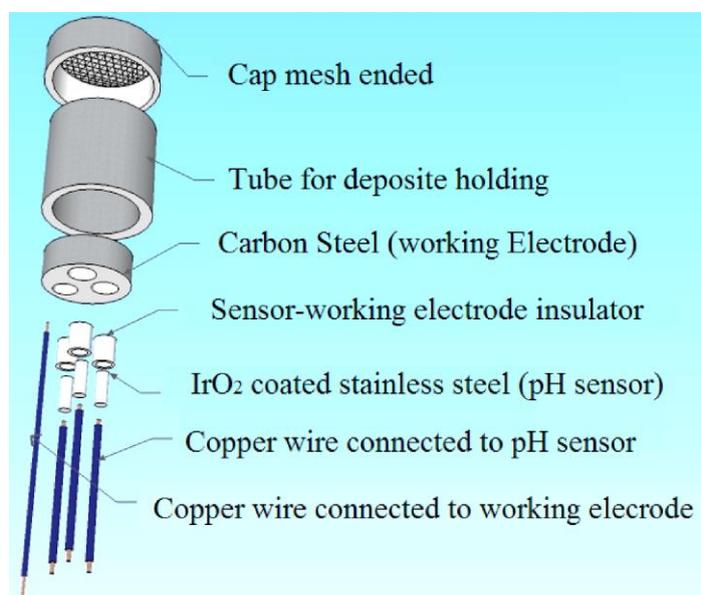
Internal pitting corrosion of X80 pipeline steel under deposited sand bed in CO<sub>2</sub>-saturated solutions was investigated by Huibin et al [13]. They used a Pt-Ir microelectrode to map the current of the specimen surface. They found that corrosion pits could begin and grow on the steel surface under a layer of sands. Corrosion pits keep growing with the increase of test time which caused a drop of local impedance and an increase of the peak current density. Besides, the increase of chloride concentration in the solution and the solution flow velocity is another reason of the corrosion pits growing.

The research focuses on design and fabrication of a novel probe for surface pH measurement under deposit. Cyclic voltammetry (CV) approach as electrodeposition method was used for forming of IrO<sub>x</sub> pH sensitive film on stainless steel substrate. Surface characterization analyses were performed to investigate the film morphology formed from corrosion process by using FESEM and EDX. The objective of the present undertaking relied on a suitable design and employment of a simple and adaptable surface pH probe for direct measurement of surface pH under deposit at a corroding surface.

## 2. EXPERIMENTAL

The electrodeposition solution was prepared by mixing 150 mg of  $\text{IrCl}_4 \cdot x\text{H}_2\text{O}$  in 100 mL of distilled water in a 200-mL glass beaker, and followed by stirring for 10 minutes for complete mixing. Then 360 mg oxalic acid was added to the solution and then stirred for another 10 minutes. Oxalic acid acts as the complex-forming agent to prevent precipitation in alkaline solutions. A 1-mL of 30% hydrogen peroxide was added, and then solution was left for 15 minutes stirring. The pH of the solution was increased slowly to pH 10.5 by adding anhydrous potassium carbonate. Addition of hydrogen peroxide to the iridium tetrachloride solution before adding  $\text{K}_2\text{CO}_3$  made the electrodeposited film smooth and lustrous. It also made it possible to deposit oxide films at lower current densities. A light green solution was obtained. The solution was allowed to age for two days at 25 °C to achieve a dark blue stable solution.

Stainless steel rods with diameter of 2 mm and length of 20 mm were used as substrates for electrodeposition of  $\text{IrO}_x$ . Electrodes were first polished with sand paper and alumina dust to achieve a surface with 0.5  $\mu\text{m}$  roughness. The electrodes were then ultrasonically cleaned with acetone and deionized water. For all electrochemical experiments, a three-electrode glass cell was used with a platinum mesh counter electrode and an Ag/AgCl (3M KCl) reference electrode for electrodeposition in cyclic voltammetry (CV). Electrodes were connected to a copper wire mechanically by using electrical cable logs, and then covered in Teflon tube to insulate all area except a circular exposed area of 3.14  $\text{mm}^2$  for electrodeposition. These electrodes embedded in a carbon steel sample which will play role of working electrode later. One extra copper wire was connected to carbon steel for LPR test simultaneously with pH measurement. Also a polymeric cap and tube were used for holding deposit as shown in Figure 1. The tube shown in this figure was filled with 5mm thick deposit (Agar). The assembled probe was exposed to  $\text{CO}_2$  containing 3% NaCl solution.



**Figure 1.** Schematic Design of pH measurement probe for monitoring of pH and corrosion under deposit (Agar)

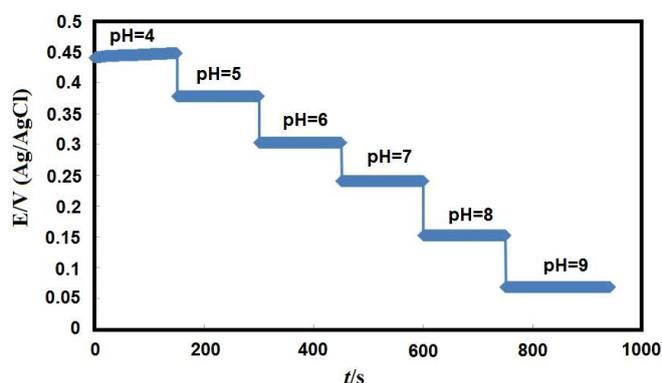
A high-performance potentiostat/galvanostat (Autolab/PGSTAT128N) was used for electrodeposition and electrochemical experiments. CV was applied for electrodeposition in a potential range of -0.5 V to 0.65 V versus Ag/AgCl (3M KCl) at various scan rates, temperatures, and cycles. A mesh Pt electrode was employed as counter electrode.

The electrodeposited iridium oxide was characterized by CV, Field Emission Scanning Electron Microscopy (FESEM) (HITACHI), and Energy-Dispersive X-ray spectroscopy (EDX). LPR and open circuit potential (OCP) techniques were used simultaneously for measuring of corrosion rate and pH, respectively. A one liter 3 wt% NaCl solution was prepared in the glass cell by mixing 30 g NaCl in 1 liter distilled water. Prior to samples immersion, the solution was purged with 1 bar CO<sub>2</sub> gas for two hours. After the solution was deoxygenated, the pH was recorded by using a glass pH sensor. It was 4 to 4.3 during experimental. After that, the working electrode was put into test solution. CO<sub>2</sub> gas purging was continued till end of experiment. The pH measurement was based on OCP method contributed with an Ag/AgCl reference electrode. Also, the corrosion rate measurements were taken for samples under Agar deposit. All experiments were conducted for 24 hours.

### 3. RESULTS AND DISCUSSION

#### 3.1. The Sensitivity of IrO<sub>x</sub> Electrode

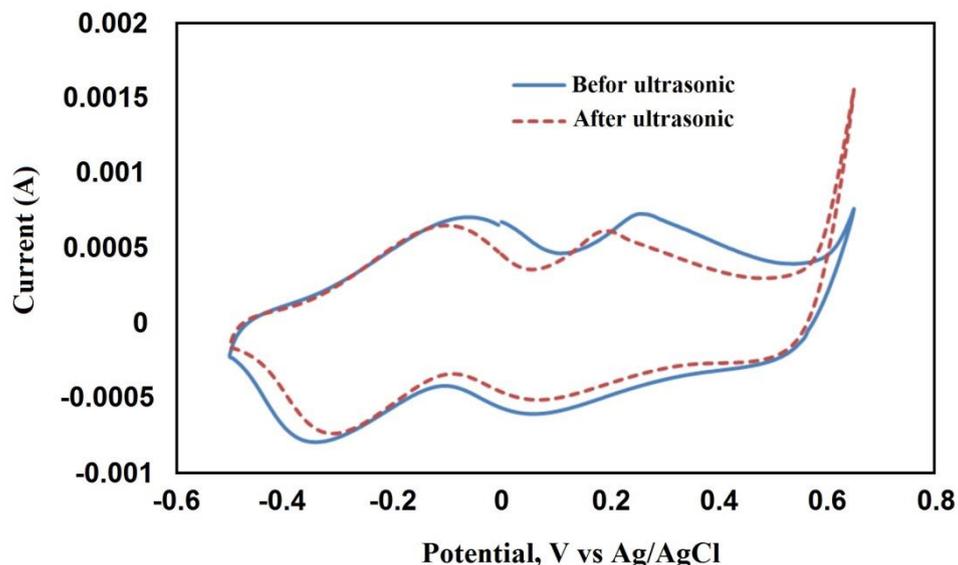
The result is depicted in Figure 2; OCP of iridium oxide electrode was plotted versus time with adjusting of pH of 100 ml universal buffer solution with 1M KOH from 4 to 9. The result shows a considerably constant buffer capacity in the mentioned pH range. The pH values of the buffer solution, showed in Figure 2, were recorded with a commercial glass electrode.



**Figure 2.** OCP response of an electrodeposited IrO<sub>x</sub> film prepared by cyclic voltammetry on stainless steel in a universal buffer while it is titrated with KOH

#### 3.2. Stability of IrO<sub>x</sub> Electrode

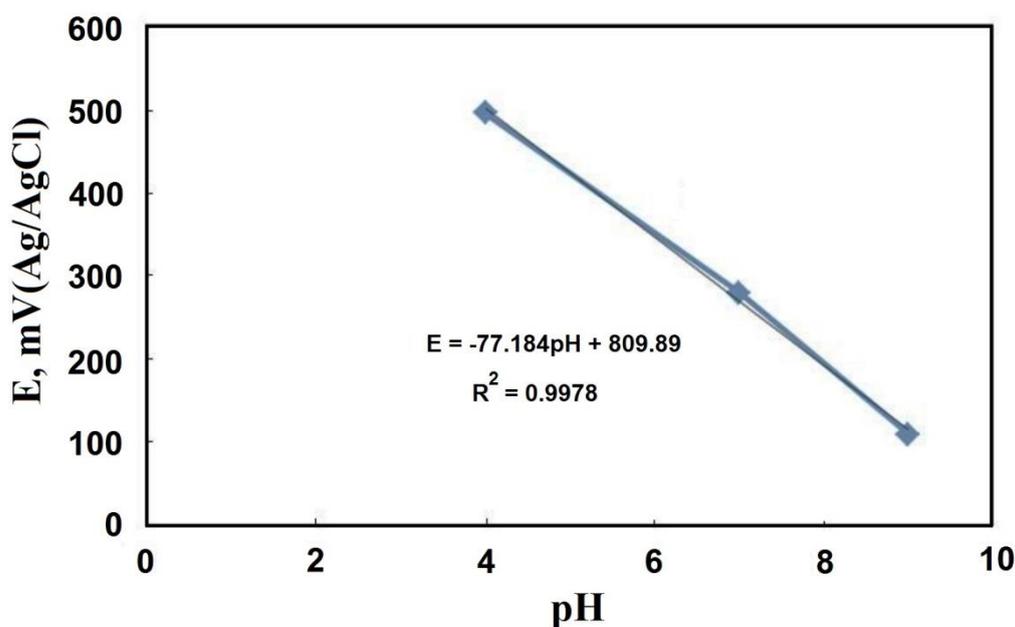
Stability is one of the essential characteristics of pH sensors. The fabricated IrO<sub>x</sub> electrode exhibited both good mechanical stability as well as electrochemical stability. Ultrasonic vibration test may cause detachment of IrO<sub>x</sub> coating from substrate which can be detected in cyclic voltammetry test.



**Figure 3.** Cyclic voltammograms of IrO<sub>x</sub> electrode before and after ultrasonic test

The cyclic voltammograms of the IrO<sub>x</sub> electrode stayed almost unchanged before and after mechanical stability tests. Only small changes in cyclic voltammogram were observed after ultrasonic vibration test. The result of ultrasonic test is depicted in Figure 3.

Many electrochemical reactions taking place in corroding metal surface under deposit consume or produce protons. The pH in the near metal surface under deposit can therefore be significantly altered during the reaction and there is a need for in situ pH measurements tracing this near surface pH under deposit.



**Figure 4.** Potentiometric response of an IrO<sub>x</sub> pH electrode in the pH range of 4–9 at a temperature of 25 °C

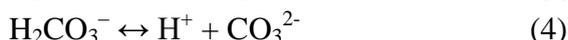
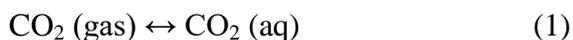
The prepared electrodeposited IrO<sub>x</sub> film showed good stability and fast response time. The electrochemical characteristics of IrO<sub>x</sub> pH microelectrodes were investigated before their application in surface pH measurement under deposit. The response of electrodeposited IrO<sub>x</sub> electrodes to exposure to a series of universal buffer solutions in the pH range between 4 and 9 is shown in Figure 4 depicts a linear super-Nernstian response resulting in a sensitivity of -77.18 mV/pH for combination of three IrO<sub>x</sub> pH sensors.

The OCP responses of the IrO<sub>x</sub> films to varying pH were experienced for two weeks. After two weeks, visual inspection under a microscope indicated no obvious signs of film delamination or degradation. Also, the OCP response of the IrO<sub>x</sub> film to varying pH remained at an average of 77 mV per pH unit with fluctuations of +/-5 mV per pH unit over the two week period.

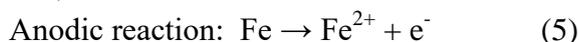
Carbon steel electrode assembled with three pH sensors covered with 5 mm Agar as deposit was exposed to CO<sub>2</sub>-saturated 3% NaCl solution. Chemical and electrochemical reaction on the carbon steel surface changed pH on the surface. Experiment was done at two temperatures; 25 and 80 °C. Furthermore, corrosion rate of carbon steel was measured by using Potentiostat in conjunction with an Ag/AgCl reference electrode.

Generally, the following reactions are observed in CO<sub>2</sub> corrosion: (a) four chemical reactions occurring in a solution and (b) four electrochemical reactions — one anodic and three cathodic — occurring on metal surfaces [14, 15]:

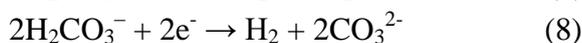
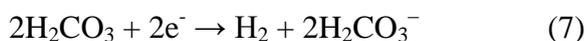
a) Chemical reactions:



b) Electrochemical reactions:



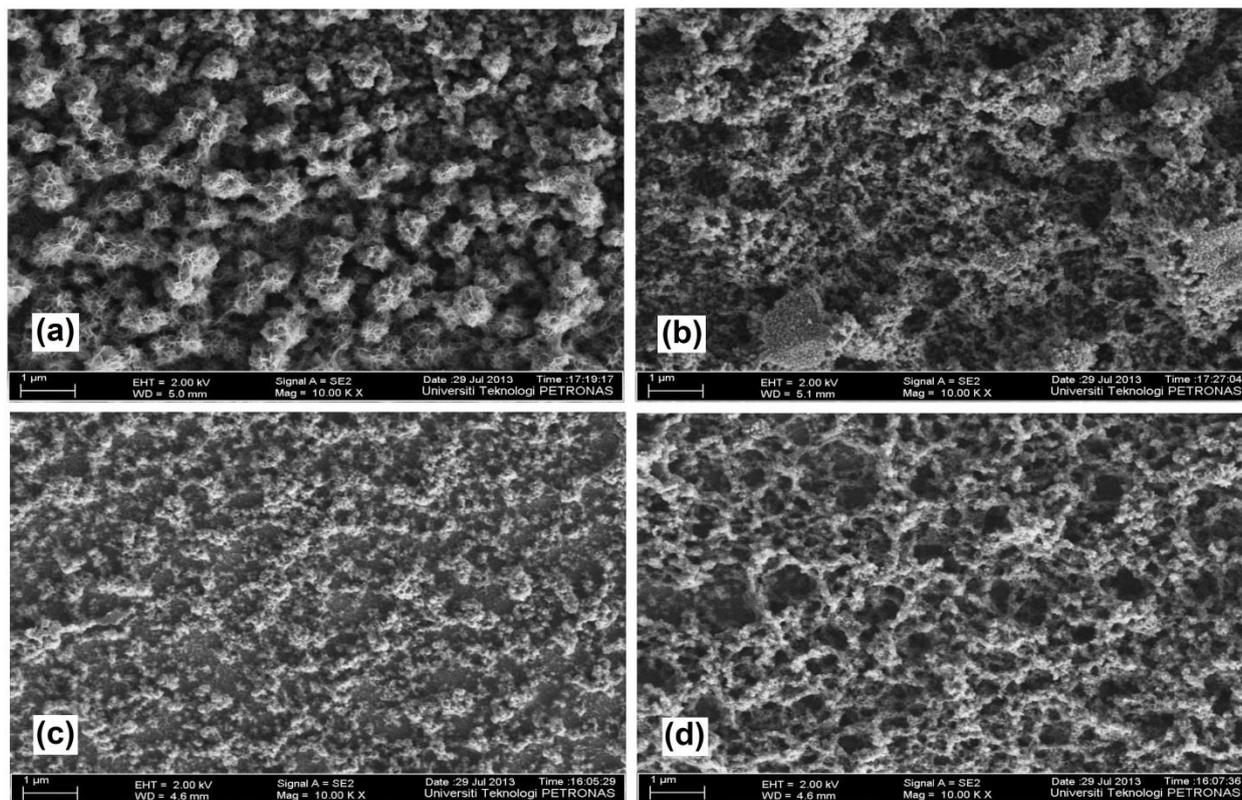
Cathodic reactions:



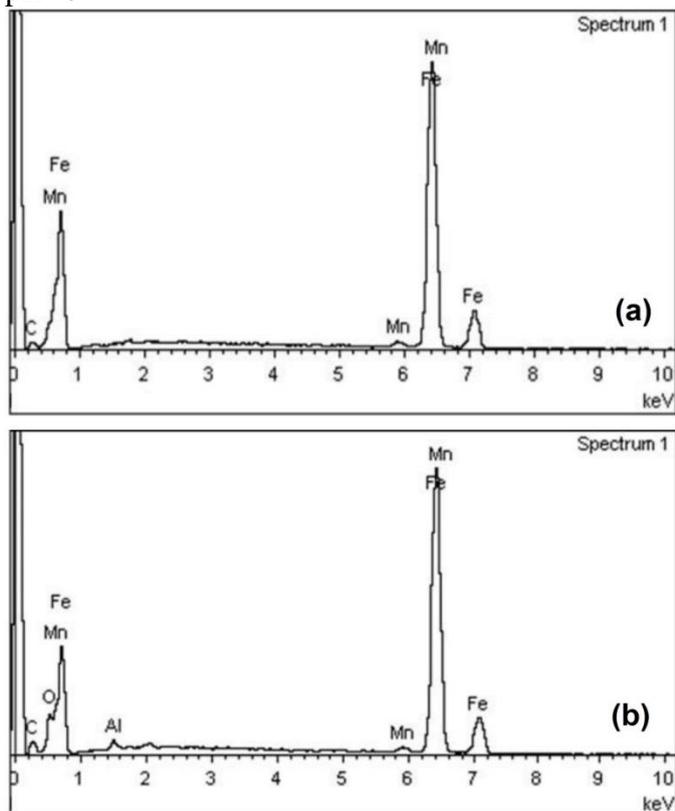
FeCO<sub>3</sub>, an insoluble corrosion product, can be formed at this stage, as follows:



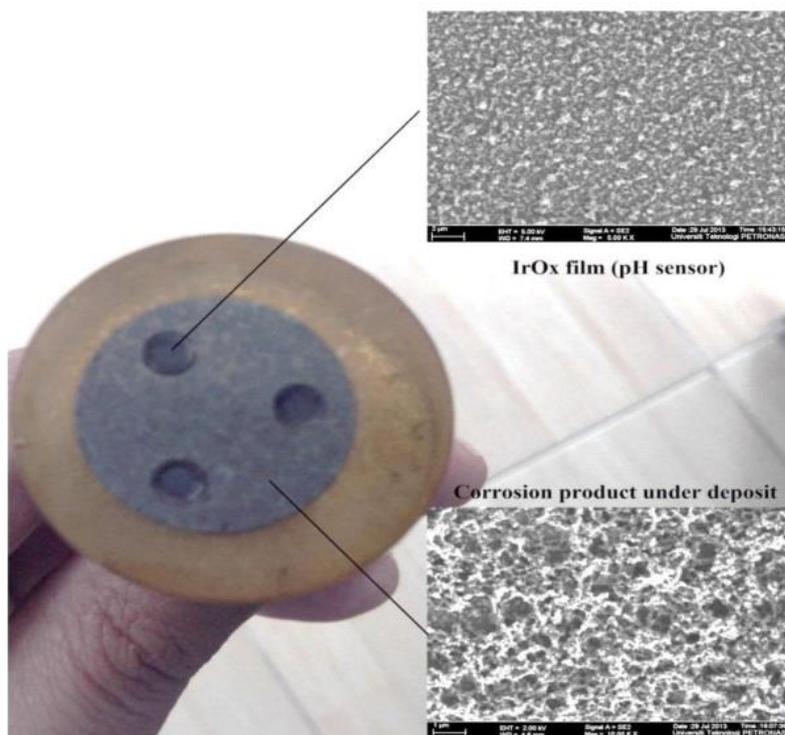
Generally, reactions of (1) to (9) also occur in metal surface under deposit, although these reactions will be limited due to difficulties in mass transport. Under deposit conditions, the deposit can be limit immigration of ions from metal surface to solution or vice versa. Then nature of corrosion process will be changed under deposit condition. Corrosion rate will be increased or decreased depend on properties of corrosion product.



**Figure 5.** FESEM images of corroded X52 carbon steel surface at 25 °C, (a) pH=4, (b) pH=6 and at 80 °C, (c) pH=4, (d) pH=6



**Figure 6.** EDX result of CO<sub>2</sub> corrosion product of X52 carbon steel at pH=6, (a) 25 °C and (b) 80 °C



**Figure 7.** Surface of pH probe and carbon steel after exposure in CO<sub>2</sub>-saturated 3% NaCl solution under deposit

### 3.3. SEM/EDX of corrosion product at three different temperatures

Figure 5 show surface morphology (face view) of the under deposit X52 steel in pH=4 and pH=6, 3% NaCl solution saturated with CO<sub>2</sub> at temperature; 25 and 80 °C, respectively. However pH condition was in favor for creating of FeCO<sub>3</sub> film, it seemed that changing in mass transport affected the nature of corrosion product.

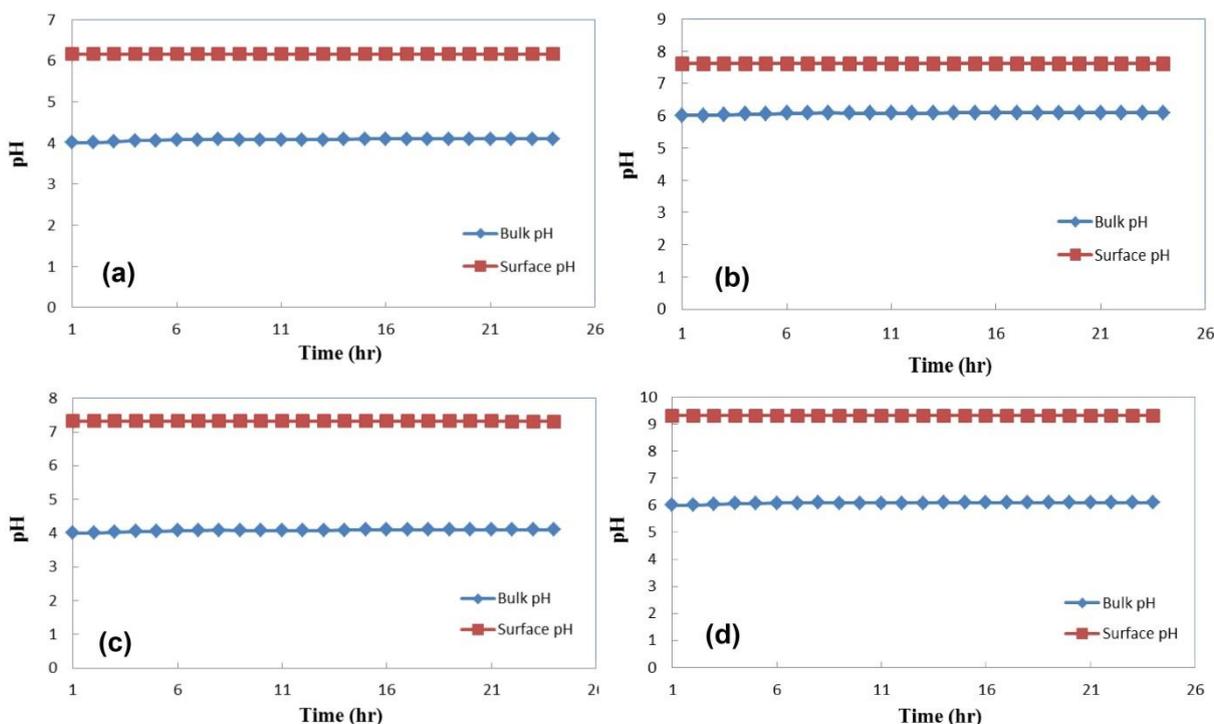
EDX results of similar samples in bulk pH=6 solution are shown in Figure 6. It can be concluded that increasing temperature and bulk pressure create a favorite condition in metal surface for FeCO<sub>3</sub> formation. In contrast, in higher surface pH and at higher temperature, the cubic crystalline shape of FeCO<sub>3</sub> was detected. The result shows that increasing temperature can increase formation of FeCO<sub>3</sub> as reported in literatures [16]. Han et al found that passive film is Fe<sub>3</sub>O<sub>4</sub> which is not a continuous film covering the steel surface, but is mainly cover boundary areas between the FeCO<sub>3</sub> crystals [17].

A top view picture of employed pH probe after experiment is shown in Figure 7 which shows surface of pH sensor is stable after CO<sub>2</sub> corrosion experiment.

### 3.4. Surface pH measurement under deposit in CO<sub>2</sub> corrosion at three different temperatures

Result of surface pH measurement at 25 °C and pH=4 is shown in Figures 8(a). A stable surface pH was reported after one hour initial variation which is nearly 2 pH units higher than the bulk pH.

The pH of metal surface under deposit increased gradually up to pH=8 after exposure in CO<sub>2</sub>-saturated 3% NaCl solution compared to the bulk solution pH (pH=6) as is demonstrated in Figure 8(b). The pH of bulk solution and metal surface were recorded every one hour for 24 hours with a normal pH probe and in-situ IrO<sub>x</sub> pH sensor embedded in carbon steel, respectively. One of the significant cathodic reactions in the CO<sub>2</sub> corrosion process is the reduction of H<sup>+</sup> ions, thus pH plays an important role in the cathodic reaction. It was reported that there is a change in the pH immediately adjacent to the electrode surface in the electrolyte and it has a main effect on the physical properties of precipitates (corrosion product) such as iron carbonate and iron sulphide [18]. Although this phenomenon will be effected by deposit due to mass transport decreasing.



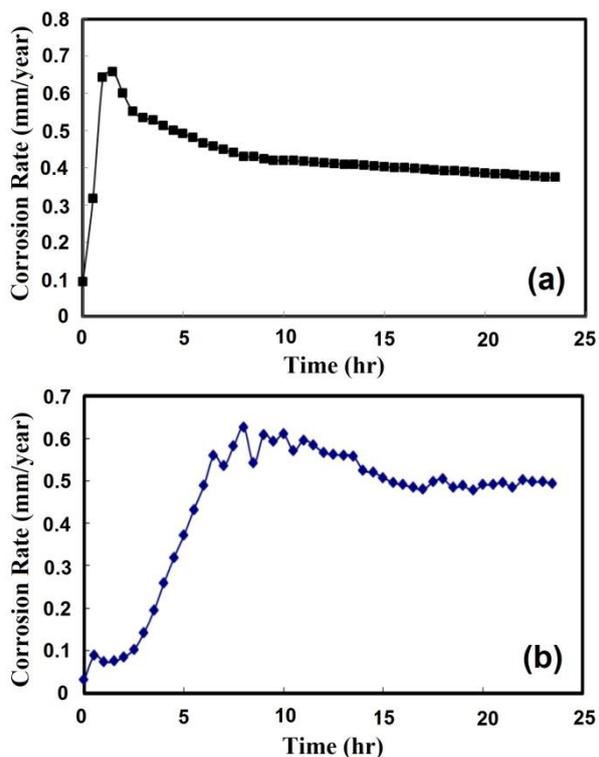
**Figure 8.** Surface pH measurement under deposit during X52 carbon steel corrosion under bulk; pCO<sub>2</sub>=0.97 bar, temperature= 25 °C, (a) pH = 4.0, (b) pH = 6.0 and pCO<sub>2</sub>=0.53 bar, temperature= 80 °C (c) pH = 4.0, (d) pH = 6.0.

### 3.5. Corrosion rate in bulk pH=4

The achieved results correspond to steady state pH values show a significant increase in surface pH values with the increase in temperature. As shown in Figure 9, corrosion rate is higher at the higher temperature due to consumption of more protons which results in a higher surface pH measurement.

Furthermore, CO<sub>2</sub> dissolves less in the solution at higher temperatures and creates a weaker buffer solution. Water chemistry model calculation shows only half of the CO<sub>2</sub> dissolves at 80 °C compared with 25 °C [12]. Both mechanisms contribute to a higher surface pH at higher temperature. Regarding to all fact discussed above, existing of agar as deposit can change mass transfer and other

chemical reaction as expected in metal surface. Result showed that surface pH values under deposit are less than same condition without deposit.



**Figure 9.** Corrosion rate of X52 carbon steel in the 3% NaCl solution at (a) 25 °C and (b) 80 °C under deposit, bulk pH=4.

Corrosion rate of X52 carbon steel under deposit was simultaneously measured at different temperature by means of another potentiostat and long term LPR approach. As can be seen from Figure 9(a), first corrosion rate increased then decreased due to formation of protective corrosion product layer. In contrast, Figure 9(b) shows corrosion rate of sample at 80 °C gradually increased and then became stable due to non-stable corrosion product film.

#### 4. CONCLUSION

A new probe design was proposed and developed with combination of pH sensors and carbon steel working electrode proposed for real-time measurement of pH on corroding carbon steel surface for better corrosion monitoring in CO<sub>2</sub> environment under deposit (agar). The pH value of the X52 carbon steel under deposit (agar) was also monitored at 25 and 80 °C. The design approves that the measurement was able to determine the pH change under agar, which is a critical requirement for studying corrosion under deposit. In all cases, metal surface pH under deposit increased compared with bulk solution pH after the corrosion process began. The results are in good agreement with theoretical prediction. IrO<sub>x</sub> pH sensor material can be changed to any other sensing material for monitoring of any

other ions in corroding surfaces which is very useful for monitoring of MIC or any other kind of corrosion.

## References

1. V. M. Tolosa, K. M. Wassum, N. T. Maidment and H. G. Monbouquette, *Biosens. Bioelectron.*, 42 (2013) 256.
2. T. Y. Kim and S. Yang, *Sens. Actuator B-Chem.*, 196 (2014) 31.
3. J. Yu, M. Khalil, N. Liu and R. Lee, *Ionics*, 21 (2015) 855-861.
4. D. O'Hare, K. H. Parker and C. P. Winlove, *Med. Eng. Phys.*, 28 (2006) 982.
5. W.-D. Huang, H. Cao, S. Deb, M. Chiao and J.-C. Chiao, *Sens. Actuator A-Phys.*, 169 (2011) 1.
6. R. Stadler, W. Fuerbeth, K. Harneit, M. Grooters, M. Woellbrink and W. Sand, *Electrochim. Acta*, 54 (2008) 91.
7. S. Kakooei, M. Che Ismail and B. Ariwahjoedi, *Int. J. Electrochem. Sci.*, 8 (2013) 3290.
8. C. M. Nguyen, W.-D. Huang, S. Rao, H. Cao, U. Tata, M. Chiao and J.-C. Chiao, *IEEE Sens. J.*, 13 (2013) 3857.
9. H. Quan, W. Kim, K.-C. Chung and J.-M. Park, *Bull. Korean Chem. Soc.*, 26 (2005) 1565.
10. Y. N. Zhang, T. L. Wang, X. Han, Z. M. Wang and J. Zhang, *Corros. Sci.*, 105 (2016) 190.
11. Y. Tan, Y. Fwu and K. Bhardwaj, *Corros. Sci.*, 53 (2011) 1254.
12. J. Han, B. N. Brown, D. Young and S. Nešić, *J. Appl. Electrochem.*, 40 (2010) 683.
13. V. Pandarinathan, K. Lepková and W. Van Bronswijk, *Corros. Sci.*, 85 (2014) 26.
14. H. J. Chung, M. S. Sulkin, J. S. Kim, C. Goudeseune, H. Y. Chao, J. W. Song, S. Y. Yang, Y. Y. Hsu, R. Ghaffari and I. R. Efimov, *Adv. Healthc. Mater.*, 3 (2014) 59.
15. P. Steegstra and E. Ahlberg, *Electrochim Acta*, 76 (2012) 26.
16. A. Mustafa, B. Ari-Wahjoedi and M. Ismail, *J. Mater. Eng. Perform.*, 22 (2013) 1748.
17. J. Zhang, Z. L. Wang, Z. M. Wang and X. Han, *Corros. Sci.*, 65 (2012) 397.
18. I. Ilim, A. Jefferson, W. Simanjuntak, M. Jeannin, Y. M. Syah, B. Bundjali and B. Buchari, *Indo. J Chem.*, 16 (2016) 198.