Short Communication

# EIS Characteristic under Cathodic Protection and Effect of Applied Cathodic Potential on Surface Microhardness of Q235 Steel

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In order to better understand the electrochemical and mechanical characterizations under different cathodic protection potentials of mild steels, the electrochemical reaction feature in the cathodic potential region was studied by electrochemical methods, surface analysis techniques and microhardness tests. Electrochemical Impedance Spectroscopy (EIS) of Q235 steel was tested at different cathodic potentials to analyze the electrochemical properties. The transfer resistance Rt with different cathodic potentials was obtained by fitting the EIS data with equivalent circuits of fitting software ZSimpwin and Zview. The relationship between Rt and potentials were also investigated. The cathodic protection potential region, best protection potential and hydrogen evolution potential were determined by Rt~E curve. Through the analysis of the cathodic polarization and microhardness relationship after hydrogen permeation, surface mechanics properties were assessed and the results showed that the cathodic protection had a significant impact on the surface mechanical properties of the steel in tidal environment.

Keywords: Q235 Steel; Cathodic Protection; EIS; Microhardness; Hydrogen Embattlement.

## **1. INTRODUCTION**

Cathodic protection has been widely used as a general anti-corrosion method for around one hundred years. The main principle of CP is to impress an external current on the material, which forces the electrode potential down to the immune region. Under cathodic protection, the potential becomes more negative and the corrosion rate of metals decreases with the increasing cathodic polarization current; Nevertheless, as the potential becomes further negative, the hydrogen evolution reaction will take place. Cathodic protection of steel in sea water under some negative potential produces hydrogen, which is likely to penetrate into the metal under high pressure or more often under an electrochemical driving force and, as a result, causes degradation of the steel. The hydrogen embrittlement will occur in industrial environment as hydrogen enters and diffuses into the steel structure inducing defects or cracks in the material matrix. A large number of researches on the interaction between hydrogen and metals have been carried out owing to their potential significance in various industrial domains.

Although lots of investigations have been conducted on the iron/hydrogen system [1–5], many problems remain unsolved. Most of earlier experiments on hydrogen embrittlement had been performed at the cathodic polarized potential where the evolution of hydrogen gas occurs [6]. Hydrogen embrittlement behavior at the adsorbed hydrogen potential ( $E_{Hads}$ ), which lies between the Ecorr and the hydrogen gas evolution potential ( $E_{H2gas}$ ), has not been widely reported [7, 8]. Moreover, few studies have been carried out by EIS, which is a very useful tool to distinguish the various processes involving complex reaction mechanisms. In addition, numerous materials with cathodic potential have been examined recently aiming to determine the critical potential that does not cause hydrogen embrittlement and the optimum cathodic protection potential by the slow strain rate test (SSRT) [9], which involves a complicated process.

In this study, in order to investigate the electrochemical reaction under cathodic potential, EIS tests were conducted in the potential range of  $-0.6V_{SCE}$  to  $-1.3V_{SCE}$ . Additionally, microhardness were measured for the specimens applied with different cathodic polarization potentials and the dependence of hydrogen absorption characteristics on applied potential was also examined for understanding the microhardness test results.

### 2. EXPERIMENTAL DETAILS

In this study, chemical composition of Q235 steel used in this paper is shown in Table 1. The steel was machined into slice specimens of dimension  $30 \times 30 \times 0.5$ mm (length×width×thickness). The work surface was ground to 800 grit silicon carbide paper, degreased with acetone, rinsed with distilled water, and dried in cool flowing air. The specimens were welded to a copper wire at one end and the other end was exposed as the working surface, then specimens were packed with epoxy resin, leaving an area of  $30 \times 30$  mm as the working surface for testing.

 Table 1. Chemical composition of the experimental steel (mass%)

C(%)	Mn(%)	Si (%)	S(%)	P(%)
0.14~0.22	0.30~0.65	≤0.30	≤0.050	≤0.045

The EIS measurements were performed using PARSTAT 2273 advanced electrochemical system. The frequency range used was from 100 kHz to 100 mHz, and the voltage amplitude was  $\pm 10$  mV rms. The working electrode corresponded to the materials used in the test. A platinum sheet was

used as the counter electrode. In addition, the saturated Colomel electrode was used as the reference electrode.

A steady state was particularly important to get relevant quantities for impedance measurements. Then, sufficiently long time is necessary to the specimen under applied potential with a steady state current.

The experiments of cathodic protection were carried out in a 3.5% (wt%) NaCl solution with a SCE as the reference electrode and platinum as the counter electrode in the potential range of  $-0.6V_{SCE}$  to  $-1.3V_{SCE}$ . Specimens with each potential in the cathodic domain were polarized for 24 hours, subsequently degreased with ethanol, and dried. The microhardnesses of the specimens were measured before and after the cathodic protection tests by an MH-6 Microhardness Tester; to ensure reproducibility of the results, five specimens were tested in each experiment performed.

## **3. EXPERIMENT RESULTS**

The EIS data were fitted with Zview and Zsimpwin to equivalent circuits used for modeling at different potentials. Micohardness were measured for 10 different locations on the specimen surface and the averaged result was acquired.

#### 3.1. Characterizations of Electrochemical impedances spectroscopy



Figure 1. EIS data of Q235 steel at different cathodic potentials.



Figure 2. Equivalent circuit, R(CR), used for generating different simulated potentials.

Before any impedance measurement, a certain period of time was required to reach a steadystate that corresponded to a steady potential. From the observed current transients in this study, a 30min delay was necessarily needed for the steel electrode to achieve a steady current before performing the EIS measurements.

Fig. 1 shows the EIS diagrams, measured for various potentials from  $-0.6V_{SCE}$  to  $-1.3V_{SCE}$  after stabilization in a 3.5% NaCl aqueous solution. It was observed that the impedance diagrams with cathodic polarization potential demonstrated a unique capacitive loop, which represents the charge transfer resistance, Rt, in parallel with the double layer capacity, Cd. The equivalent circuit R(CR) is given in Fig.2: Rs indicates the solution resistance, Cd the double layer capacity and Rt the the charge transfer resistance. It can be chiefly concluded that the charge transfer resistance is dependent on the cathodic polarization potential.



Figure 3. Rt~E curve measured at various potentials

Fig. 3 shows the values of Rt at various potentials from  $-0.6V_{SCE}$  to  $-1.3V_{SCE}$  after stabilization in a 3.5% NaCl aqueous solution. From the trends of the RT values, within the said range, at slightly negative potentials ( $-0.6V_{SCE}$  to  $-0.75V_{SCE}$ ), Rt increased with the decreasing cathodic polarization potential. At relatively negative cathodic polarization potentials( $-0.75V_{SCE}$  to  $-1.05V_{SCE}$ ) a significant decrease of the Rt value was observed as the potential decreased. and then, Rt decreased dramatically with the decreased potential and finally dropped towards  $0 \Omega \cdot cm^2$ .

#### 3.2. Surface Microhardness with different cathodic potentials

The measured microhardness values for various potentials are given in Fig. 4. It is shown that the microhardness of Q235 steel without cathodic protection was in the range of 160-170 Mpa. For the steel under the potential positive than -0.9  $V_{SCE}$ , the microhardness value was nearly constant, which was in agreement with Q235 steel with no cathodic polarization. As the potential decreased, only a very small increase in the microhardness was observed. For a more negative potential (smaller than - 1.0  $V_{SCE}$ ), the microhardness value significantly increased. When at the potential relatively negative than -1.2  $V_{SCE}$ , the microhardness value dropped dramatically to a level which was lower than that of Q235 steel with no cathodic polarization potential applied.



Figure 4. The measured Vickers Hardness values under various potentials

#### 4. DISCUSSION

The hydrogen permeation potential of the Q235 steel electrode was investigated with the charge transfer resistance, as well as with the change of microhardness values with different cathodic polarization potentials.

Fig. 1 shows the impedance diagrams of Q235 steel applied with different cathodic potentials, the electrical equivalent circuit R(CR) given in Fig. 3 was proposed[11].

High-frequency domain (left) of the impedance, which provides the information of corrosion product on the electrode surface, were almost the same while the low-frequency domain (right), which corresponds to the electrode reaction, changed significantly.

For the low-frequency part, Rt changes regularly with the cathodic polarization potential [12]. At the Ecorr potential, two electrode reactions, i.e. anode reaction and cathode reaction, occur at the same time and therefore, the impedance measured in cathodic polarization potential is the comprehensive response to the anode and the cathode.

At the mixed potentials when anodic and cathodic reactions occur simultaneously [13], he anodic and cathodic reactions occurring at the surface of steel are oxidation of iron and the reduction of oxygen and water, respectively:

$$Fe \rightarrow Fe^{2+}+2e$$
(1)  

$$O_2+2H_2O+4e \rightarrow 4OH^{-}$$
(2)  

$$H_2O+e \rightarrow H+OH^{-}$$
(3)

In particular, at less negative potentials, the oxygen reduction dominates the cathodic process[14], while hydrogen evolution dominates at more negative potentials. Therefore, application of cathodic protection would affect the cathodic process and local electrochemical environment as well as the anodic behavior of steel.

The most hydrogen atoms got from the cathodic process may encounter each other and immediately combine into H2 gas molecules and get off, but a portion of the hydrogen atoms enter the surface and remain as individual atoms in the metal[15]. When a sufficient amount of hydrogen concentrates in the steel, the property of the steel is deteriorated by interstitial hydrogen atoms[16]. The subsequent discussion is about the change of charge transfer resistance and the microhardness along with the change of cathodic polarized potential.

The charge transfer resistance of the impedance, Rt, can be written as:

 $1/Rt = 1/Rt_a + 1/Rt_c$  (4)

Fig.5 shows the equivalent circuits used for modeling at mixed potential. Where  $Rt_a$  is the transfer resistance of anode reaction and  $Rt_c$  the transfer resistance of cathode reaction. When applied with the cathodic polarization potential,  $Rt_a$  increases as the potential became more negative while  $Rt_c$  diminished slowly since the latter was controlled by oxygen electrochemical activation process. When  $Rt_a$  is much larger than  $Rt_c$ , the anode reaction fraction is very small. And cathode reaction is the main reaction on the electrode surface. Therefore, as the Rt reaches the peak value, the cathodic polarization potential is considered the best protection potential, the value of which for Q235 steel was -0.75V<sub>SCE</sub>.



Figure 5. Equivalent circuit used for modeling at mixed potential

In addition, when the cathodic polarization potential achieves a certain negative level, the cathodic evolution reaction of hydrogen occurs along with oxygen reduction reaction. The equivalent circuit used for modeling at cathodic polarization potential is shown in Fig.6.  $Rt_c$ , the transfer resistance of cathode, can be written as:

 $1/Rt_c = 1/Rt_o + 1/Rt_H$  (5)

Where Rto is the transfer resistance of oxygen reduction reaction and RtH is the transfer resistance of hydrogen evolution reaction. When the cathodic reaction in the hydrogen evolution reaction constitutes a small proportion,  $RtH \rightarrow \infty$ , Rtc is approximately equal to the cathodic reduction of oxygen reduction reaction resistance Rto. Along with the transport of oxygen in the solution, Rtc decreased as the electrode potential became negative, which is shown by the slope of Rt~E curve. When hydrogen evolution reaction is significant, RtH became smaller. RtH, together with Rto reacted on upon Rtc. Rtc decreases rapidly as a result of the impact of RtH, forming a turning point in the Rt~E curve. The cathode potential of the inflection point indicates a hydrogen evolution reaction potential. For Q235 steel, at the potential of -1.05 VSCE, hydrogen evolution reaction occurs. Fig.4 shows the change of microhardness with potential. For relatively positive potential ranging from -0.7VSCE to -0.9VSCE, no significant change was noted in the microhardness when compared with steel without cathodic polarization potential. As the potential decreases, entering the range of -1.0VSCE to -1.1VSCE, the microhardness showed an obvious increase, which indicated that the brittleness of materials intensified. For even negative potentials (more negative than -1.1 VSCE), Rt becomes extremely small, implying that hydrogen evolution reaction arises fiercely and hydrogen permeation occurs. Therefore the performance of the microhardness at the protection potential of -1.0VSCE also shows that hydrogen embrittlement may be occurred for the specimens. For even more negative potentials than -1.2VSCE, the microhardness value of specimen dropped significantly. On the surface of the specimen, large amounts of hydrogen bubbles were observed. Hydrogen penetrated into specimen under the electrochemical driving force, which will cause deterioration of the mechanical properties of the steel. At the potential of -1.0VSCE, hydrogen permeation will be occurred. Consequently, the most negative protection potential for cathodic protection is the potential of hydrogen evolution reaction occurs, the value of which for Q235 steel is -1.0 VSCE.



Figure 6. Equivalent circuit used for modeling under cathodic polarization

# **5. CONCLUSIONS**

Based on the results acquired in this study, the following conclusions can be obtained.

(1) The Rt~E curve was get with EIS under different cathodic protection potential for Q235 steel in this paper. The cathode potential of the inflection point of Rt~E curve indicates a hydrogen evolution reaction potential. The most negative protection potential for cathodic protection is -1.05  $V_{SCE}$  for Q235 steel. As the Rt reaches the peak value, the cathodic polarization potential is considered the best protection potential, the value of which for Q235 steel was -0.75V<sub>SCE</sub>.

(2) The microhardness of Q235 has no significant change under the cathodic protection potentials from  $-0.7V_{SCE}$  to  $-0.9V_{SCE}$ , and increased under negative potential than  $-0.9 V_{SCE}$ . For even more negative potentials than  $-1.15V_{SCE}$ , the microhardness values of specimen dropped significantly.

(3) The cathodic protection potential for Q235 should not lower than  $-1.0V_{SCE}$ .

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