

Semiconducting Behavior of Carbon Steel in Electrolyte Solution

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Abstract: In this paper, the semiconducting behavior of carbon steel in acid, base and salt solutions was studied by utilizing potential-capacitance and Mott-Schottky analysis. It was pointed out that the capacitance variation of space charge layer of carbon steel in different solution was different. The carbon steel showed p-type semiconducting behavior in 5% sulfuric acid and 5% sodium sulfate solution. However, the carbon steel showed n-type semiconducting behavior in 5% sodium hydroxide. It was suggested that the space charge layer of the carbon steel in different electrolytes might be asymmetric.

Keywords: Carbon steel, conducting mechanism, p-type semiconductor, n-type semiconductor.

1. INTRODUCTION

It is well known that stainless steels and the film have drawn much concern for almost 170 years [1]. It still represents a special and favorite topic for electrochemists and material scientists on this topic [2-21]. In general, passive film on the surface of stainless steel could be interpreted in terms of a semiconductive film. Capacitance measurements and photoelectrochemistry are often utilized to study the conducting behavior of passive films and to obtain the donor density (N_D) and the flat band potential (E_{fb}) by analysis of Mott-Schottky plots [11, 22-26]. The results suggested the passive film over the stainless steel which exhibits an n-type semiconductor with high density of $10^{25} \sim 10^{27} \text{ m}^{-3}$. The capacitance measurements at different frequencies indicated that the passive film was amorphous or a strongly disordered semiconductor. Simoes *et al.* observed that Mott-Schottky plots of passive films formed on 304 stainless steel were nonlinear [22].

Theoretical studies of mechanism of this kind of semiconducting film have been well investigated in the classic theory of solid state physics. Electron transport through such film can be affected by two mechanisms: If the film is highly doped with electron donors or acceptors, the electrons are transported *via* the conduction or the valence band. In heavily disordered films, which have a high concentration of localized electronic states in the band gap, electron transfer through the film can occur by a series of hops between such states; this is a so-called hopping conductivity mechanism. Many models have been used to study and describe these disordered systems such as ion implantation [27,28], passive film [29,32], and polymer films with localized electronic states [30] etc. Hopping conductivity in disordered systems is also well documented [31]. In addition, Clayton *et al.*

observed the evidence for a bipolar mechanism of passivity in Mo bearing stainless steels [33].

A large amount of research has been performed on stainless steel [11, 22-26] and metals including beryllium [34], aluminum [35], titanium [36], zinc [37], gallium [38], copper [39], nickel [40], tungsten [41] etc. to study the electronic structure and semiconductive properties of passive film. In our previous study of temporarily protective oil coating (TPOC) on its electrochemical inhomogeneity [41-45], voltammetric investigation suggested the potential variation of oil coating during its degradation. At the early stage of immersion, anodic reaction was a rate-determining step in the overall reaction in metal/oil/electrolyte system, which has a potential to shift positively with varying immersion time. After being immersed for some time, the potential of oil coating shifted towards corrode direction with increasing immersion time; at this stage ionic diffusion in the coating was predominant [42].

Previous studies of capacitance measurement with Mott-Schottky analysis showed that on the surface of AISI 304 stainless steel, the temporarily protective oil coating behaved as a semiconductor during its degradation. With the increasing immersion time, temporarily protective oil coating transformed from p-type semiconductor at the early stage of immersion to n-type semiconductor [46].

Though there are some studies on the electric and electronic structure of carbon steel [47-49], little work has been done in semiconducting behavior of carbon steel in different electrolyte. In this paper, we utilized capacitance measurement with Mott-Schottky analysis to study the conducting behavior of carbon steel in 5% sulfuric acid, 5% sodium sulfate and 5% sodium hydroxide solutions varying with immersion time.

2. EXPERIMENTAL

The electrode samples prepared in this paper were made of a carbon steel rod containing 0.20 wt% C, named as No.20 carbon steel by Chinese Standard having a diameter of

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10mm. The working electrode was embedded in an epoxy resin, resulting in an exposed steel area of 0.785cm^2 . The working surface of the electrode was polished with emery paper to 800 grit, degreased with acetone, and then the electrode was separately immersed in a 5%(w/w) sulfuric acid, 5%(w/w) sodium sulfate and 5%(w/w) sodium hydroxide solution for capacitance measurement. The solutions were made from analytical grade reagent and distilled water. All tests were carried out at ambient temperature.

All testing electrode samples were introduced in a conventional three-electrode electrochemical cell. The capacitance of electrode sample was measured at 1000 Hz in the potential range -0.5V to 0.5V by performing a potential scan in the positive direction with a computer-controlled Electrochemistry Station Model CHI660C. The reference electrode was a saturated calomel electrode (SCE), and a platinum wire was used here as the counter electrode.

The Mott-Schottky relationship of $(1/C_{sc})^2$ vs U expressed the potential dependence of C_{sc} of a semiconductor electrode under the depletion condition, for n-type semiconductor,

$$\frac{1}{C_{sc}^2} = \frac{2}{\epsilon\epsilon_0 e N_D} (U - U_{fb} - \frac{kT}{e})$$

For p-type semiconductor,

$$\frac{1}{C_{sc}^2} = -\frac{2}{\epsilon\epsilon_0 e N_A} (U - U_{fb} - \frac{kT}{e})$$

where C_{sc} is space charge capacitance, ϵ is the dielectric constant of the charge layer for carbon/electrolyte, ϵ_0 is permittivity of free space ($8.854 \times 10^{-12}\text{F/m}$), e is the charge of electron, N_D and N_A are density of donor and acceptor respectively, U_{fb} is flat band potential, k is Boltzmann constant, T is absolute temperature.

A set of impedance values of all electrode samples varied with potential and immersion time were also obtained from capacitance measurements.

3. RESULTS AND DISCUSSION

3.1. Capacitance Variation of No.20 Carbon Steel During its Degradation in Different Electrolyte

The capacitance-potential curves of electrodes showed capacitance variation with immersion in different electrolyte solution (Figs. 1,3). For No.20 carbon steel in 5% sulfuric acid solution (Fig. 1), with increasing potential, the capacitance increased. The variation of capacitance may be due to a decreasing thickness of the depletion layer and increasing number of charge carriers (donor for an n-type semiconductor) [47]. For No.20 carbon steel in 5% sodium sulfate solution (Fig. 2), the capacitance increased. This phenomenon for variation of capacitance could be interpreted as a decreasing thickness of the depletion layer and increasing number of charge carriers. For the two kinds of electrolytes, with increasing immersion time, the capacitances had the inclination of increasing gradually, these may be due to ionic diffusion and penetration in the space charge layer on the surface of the carbon steel in the electrolytes, and due to increasing number of charge carriers.

However, for the electrolyte of 5% sodium hydroxide solution, the results were different. For No.20 carbon steel in

5% sodium hydroxide solution (Fig. 3), there were two valleys in the capacitance-potential plot. The peaks of valleys were at the potential of -0.3V vs SCE and 0.4V vs SCE respectively. With increasing potential, the capacitance had a decreasing trend. The variation of capacitance may be due to increasing thickness of the depletion layer and decreasing number of charge carriers. With increasing immersion time, the capacitances had an inclination of increasing gradually, these may be due to ionic diffusion and penetration in the space charge layer on the surface of the carbon steel in the electrolyte, and then increasing number of charge carriers. When the potential was higher than 0.4V vs SCE, the capacitance began to increase sharply.

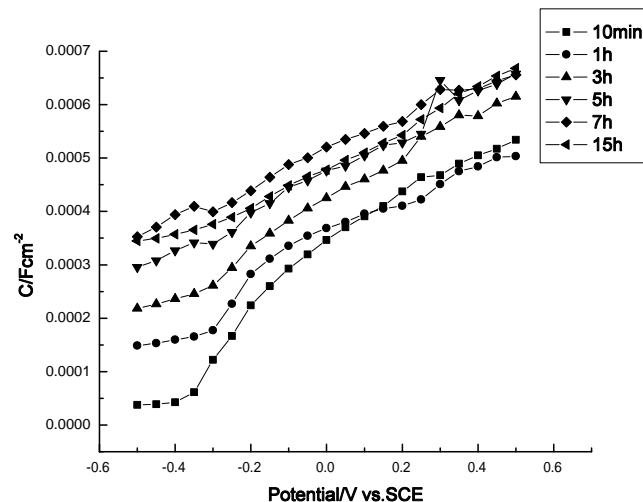


Fig. (1). The capacitance-potential curve of No.20 carbon steel obtained at 1000Hz with different immersing time in 5% sulfuric acid solution.

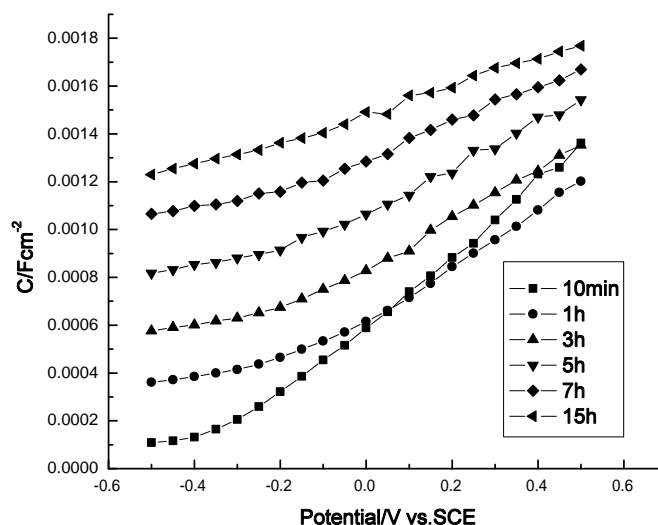


Fig. (2). The capacitance-potential curve of No.20 carbon steel obtained at 1000Hz with different immersing time in 5% sodium sulfate solution.

3.2. Analysis of Mott-Schottky Plot for Carbon Steel During its Degradation in Different Electrolyte

The charge distribution at the semiconductor and electrolyte interface was often determined by measuring the capaci-

tance of the space-charge layer (C_{sc}) as a function of the electrode potential (U).

We calculated the values of $(1/C_{sc})^2$ of the carbon electrode and plotted with the potential shown in Figs. (4,6).

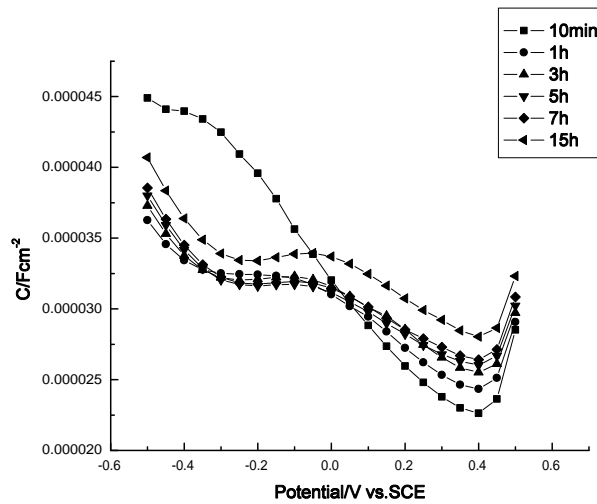


Fig. (3). The capacitance-potential curve of No.20 carbon steel obtained at 1000Hz with different immersing time in 5% sodium hydroxide solution.

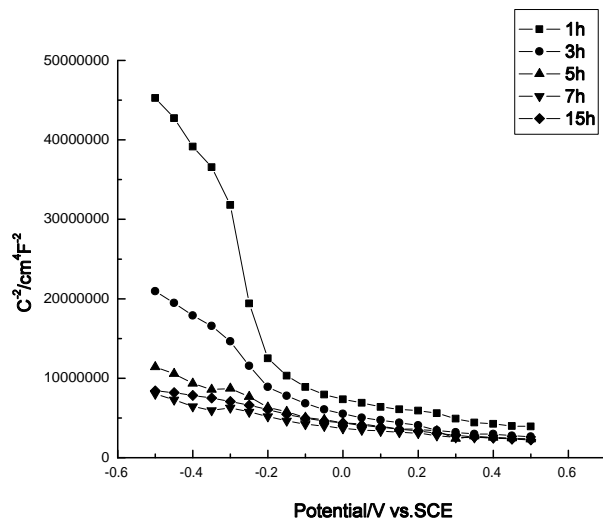


Fig. (4). The Mott-Schottky plot of No.20 carbon steel obtained at 1000Hz with different immersing time in 5% sulfuric acid solution.

For No.20 carbon steel in 5% sulfuric acid solution (Fig. 4), the Mott-Schottky curve was nonlinear with immersions of 1 hour and 3 hours. This was the same as that of paper [22]. With increasing immersion time, Fig. (4) depicted a linear correlation between values of $(1/C_{sc})^2$ and the potential of the electrode in 5% sulfuric acid solution at the potential range of $-0.5V \sim 0.5V$. The depletion layer behaved as a p-type semiconductor (negative slope), and the slope of the Mott-Schottky plot decreased gradually. This suggested that with increasing immersion time, acceptor of density (N_A) increased gradually.

For No.20 carbon steel in 5% sodium sulfate solution (Fig. 5), the Mott-Schottky curve was linear with immersion time. Fig. (5) depicted a linear correlation between values of $(1/C_{sc})^2$ and the potential of the electrode in 5% sodium sulfate solution at the potential range of $-0.5V \sim 0.5V$. The de-

pletion layer also behaved as a p-type semiconductor (negative slope), and the slope of the Mott-Schottky plot decreased gradually. This suggested that with increasing immersion time, acceptor of density (N_A) increased gradually. This situation was different with the passive film of carbon steel prepared in the atmosphere, which showed n-type semiconductor [47-49].

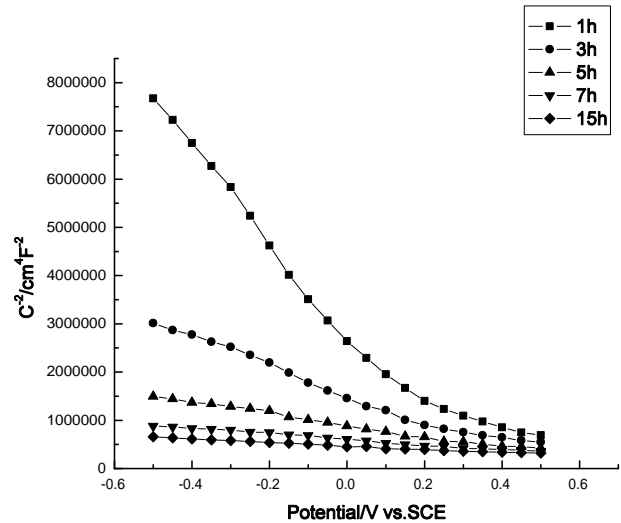


Fig. (5). The Mott-Schottky plot of No.20 carbon steel obtained at 1000Hz with different immersing time in 5% sodium sulfate solution.

Fig. (6) showed the results of the capacitance measurements of the No.20 carbon steel in 5% sodium hydroxide solution, plotted as C^{-2} vs potential (U). Two linear regions revealing Mott-Schottky behavior could be attributed to the development of depletion layers promoted by band bending. For No.20 carbon steel in 5% sodium hydroxide solution (Fig. 6), there were two peaks in the Mott-Schottky plot. The peaks were also at the potential of $-0.3V$ vs SCE and $0.4V$ vs SCE, respectively compared with the Fig. (3). At the potential range of $-0.5V \sim -0.3V$ vs SCE and $0V \sim 0.4V$ vs SCE, Fig. (6) depicted a linear correlation between values of $(1/C_{sc})^2$ and the potential of the electrode in 5% sodium hydroxide solution. The depletion layer of the carbon steel, however, behaved as an n-type semiconductor (positive slope), and the slope of the Mott-Schottky plot had the inclination of decreasing gradually. This suggested that with increasing immersion time, donor of density (N_D) increased gradually. Compared with the values of $(1/C_{sc})^2$ shown in Figs. (4,6), it was obvious that N_D of the carbon steel in 5% sodium hydroxide was three orders of magnitude higher than that of N_A in 5% sulfuric acid and 5% sodium sulfate, respectively. Considering the ions (including cation or anion) in the electrolyte could not change the ϵ (the dielectric constant of the charge layer for carbon/electrolyte) so sharply, thus this situation might be due to asymmetry of carbon/electrolyte system for different solution.

In our previous study of metal/oil coating/electrolyte system [50], it was pointed out that at the early stage of immersion of oil-coated metal specimen, the electrochemical reactions in metal/coating/electrolyte system were very small, the amount of metal cation produced at the metal/coating interface was ultra small, and the amount of corresponding anion creating at the coating/electrolyte was very small. These ions

could not diffuse through the coating and constructed steady diffusion passway in the oil coating. At this time, only electron could transfer through the coatings by electrons hopping the localized electronic states in organic coatings. Electrochemical reaction in the metal/coating/electrolyte system was determined by any one-step, which directly related to metal cation formation and transmission in the metal/coating/electrolyte system. At this time, oil coating behave as a p-type semiconductor. However, the density of N_A was very small.

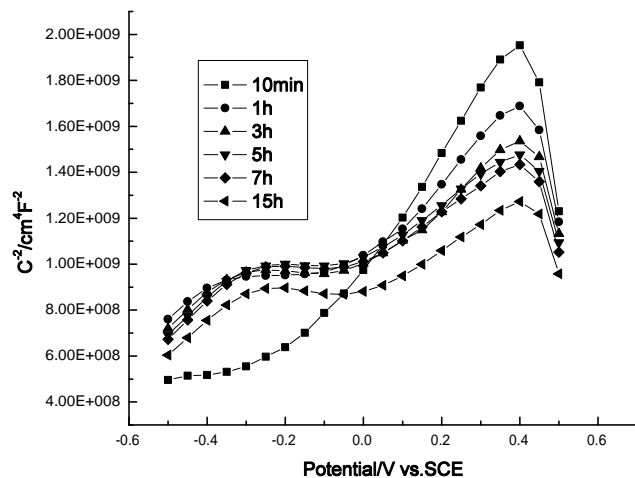


Fig. (6). The Mott-Schottky plot of No.20 carbon steel obtained at 1000Hz with different immersing time in 5% sodium hydroxide solution.

With the increase of immersion, ions in the electrolyte began to diffuse in the oil coating, and gradually constructed the steady diffusion layer in the coating. At this time, electrochemical reaction in the metal/coating/electrolyte system was determined by any one step concerning with electron transmitting in the overall reaction of metal/coating/electrolyte system. Considering the steps of cation producing and transmitting in the oil coating was in equilibrium, in order to keep the charge equilibrium in the oil coating and prevent charge accumulation in the metal/coating/electrolyte system, the amount of cations producing at the metal/coating interface and transmitting through the coating were equal to the amount of anion producing of the cathodic reaction (oxygen reduction, $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$) at coating/electrolyte interface.

From above analysis, it was clear that cathodic processes concerning with the electron production, electron transmitting in the coating and electron consuming at coating/electrolyte interface were predominant, whereas anodic processes in the metal/coating/electrolyte were in equilibrium. At this time, oil coating behaved as an n-type semiconductor, and the density of N_D was much higher than that of N_A , which the oil coating being at the early stage of immersion.

For the mechanism analysis of metal/oil coating system in the same salt solution, in metal/oil coating/electrolyte system, N_D was much higher than that of N_A , the space charge layer in the system was asymmetric with time. However, for the carbon steel in different electrolyte at the same time, N_D of the carbon steel/electrolyte fast electrochemical system

was much higher than that of N_A , this was the same as that of metal/oil coating/electrolyte system. It was suggested that the space charge layer in the carbon/electrolyte system might be asymmetric for different solution.

CONCLUSION

The results of our investigations had led to the following conclusions:

- 1) The capacitance variation of space charge layer of No.20 carbon steel in different solution was different;
- 2) The carbon steel showed p-type semiconducting behavior in 5% sulfuric acid and 5% sodium sulfate solution;
- 3) The carbon steel showed n-type semiconducting behavior in 5% sodium hydroxide. 4) The space charge layer of the carbon steel in different electrolyte might be asymmetric.

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