

Influence of calcium nitrite on the passive films of rebar in simulated concrete pore solution

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Abstract

Purpose – This paper aims to study the influence of the addition of calcium nitrite on the passive films of rebar to reveal what causes calcium nitrite to further prolong the durability service life of the reinforced concrete structures.

Design/methodology/approach – A comprehensive experimental study of the passive films, such as components, surface morphologies, electric structure and compactness, was carried out in a saturated calcium hydroxide solution which is normally used to simulate concrete pore solution by using X-ray photoelectron spectroscopy, atomic force microscopy, Mott–Schottky and potentiostatic polarization, respectively.

Findings – The results showed that the passivation behavior of rebar has been changed dramatically by the addition of calcium nitrite. That is, the passive film formed in the solution with the addition of 10 g/L $\text{Ca}(\text{NO}_2)_2$ had less donor density (Nd), more positive plat potential, smoother surface and lower content of $\text{Fe}_{\text{hydrox}}$ than that formed in the solution without $\text{Ca}(\text{NO}_2)_2$.

Originality/value – The study focuses on the passive films and provides a more clear cognition of the durability service life extension of the reinforced concrete structures caused by the addition of calcium nitrite.

Keywords AFM, XPS, Calcium nitrite, Passive films, Rebar

Paper type Research paper

1. Introduction

Chloride ions are the cause of local depassivation of the rebar, leading to pitting corrosion, which could result in the cracking and spalling of the concrete cover, thus leading to an overall loss in structural integrity. The prevention and treatment of this problem can be addressed by several methods, including concrete sealers, realkalization, cathodic protection and corrosion inhibitors (Broomfield, 1997).

Compared with other preventive methods, corrosion inhibitors seem to be more attractive because of their low cost and easy handling (Bertolini *et al.*, 2004). Nitrite inhibitor is the most commonly used in concrete projects to improve its durability, and this has been investigated by many researchers (Song *et al.*, 2009; Sideris and Savva, 2005; Gonzalez *et al.*, 1998; Rosenberg and Gaidis, 1997; Ann and Song, 2007; Ramasubramanian *et al.*, 2001; Mnmoliti *et al.*, 1999; Hope and Ip, 1989; Liu *et al.*, 2004; Qiao *et al.*, 2010; Ann *et al.*, 2006; Królikowski and Kuziak, 2011; Blanksona and Erdem, 2015; Sangoju *et al.*, 2015; Cao *et al.*, 2015). Ramasubramanian *et al.* (2001) studied the influence of calcium nitrite on the corrosion behavior and concluded that calcium nitrite could inhibit the rebar corrosion. Mnmoliti

et al. (1999) investigated the effect of nitrite ion on the critical chloride ion concentration of pitting corrosion. It could heighten the critical chloride ion concentration and delay the pitting corrosion time of the rebar. The critical chloride ion concentration of pitting corrosion is dependent on the value of calcium nitrite. Hope and Ip (1989) reported that the value of $\text{NO}_2^-/\text{Cl}^-$ was between 0.07 and 0.09 in concrete simulated pore solution. Liu *et al.* (2004) discussed that the mole rate of $\text{NO}_2^-/\text{Cl}^-$ was larger than 0.32 in concrete simulated pore solution (pH = 12.6). Qiao *et al.* (2010) investigated that the mole rate of $\text{NO}_2^-/\text{Cl}^-$ was larger than 0.4 in concrete simulated pore solution (pH = 12.5). The mole rate of $\text{NO}_2^-/\text{Cl}^-$ is also studied in concrete. Ann *et al.* (2006) research result has shown that the mole rate of $\text{NO}_2^-/\text{Cl}^-$ is between 0.34 and 0.66. Some results showed that the value was between 0.5 and 1.0. All the above results indicate that the nitrite inhibitors could heighten the critical chloride ion concentration and inhibit the corrosion of rebar. It has been known that steel embedded in concrete or concrete simulated pore solution is in the passive state because of the high basicity of this medium. Passive films would form on the surface of the rebar. It would decide the corrosion behaviors of the rebar,

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especially the resistance of the pitting corrosion (Liu *et al.*, 2007). Therefore, the increase in the critical chloride ion concentration of the pitting corrosion caused by the addition of nitrite is due to the property exaltation of the passive films. To the authors' knowledge, there is little information available in literature about the passive films of rebar with the nitrite added.

In this paper, the influences of calcium nitrite on the passive films of the rebar were investigated in simulated concrete pore solution. It would provide a more clear cognition of the durability service life extension of the reinforced concrete structures caused by the addition of calcium nitrite.

2. Experimental

2.1 Materials

The cylinder samples of carbon steel, with a length of 10 mm and a diameter of 10 mm, were sealed in epoxy resin with an exposed working area of 0.785 cm². The nominal composition of the carbon steel is listed in Table I. Also, the metallographic phase of the carbon steel, obtained by a polarizing microscope, is shown in Figure 1. As can be seen, the grain size is about 50 μm. The saturated calcium hydroxide solution (designated as "CH") is used as surrogate to simulated concrete pore solution in this work (Ghods *et al.*, 2011). The pH value of the CH solution is 12.6. For the saturated calcium hydroxide solution with the addition of 10 g/L Ca(NO₂)₂, it is designated as "CH-CN". The analytical reagents of Ca(OH)₂, Ca(NO₂)₂, and NaCl are used for solution preparation in the work.

2.2 Electrochemical measurements

A three-electrode system used for all electrochemical measurements was composed of the rebar as the working electrode, mixed metal-metal oxides-coated Ti anode as the counter electrode and saturated calomel electrode (SCE) as the reference electrode. All potential values reported in this paper are vs SCE. The test mediums are the CH and CH-CN solutions. The testing temperature is about 20 ± 2°C. Before the experiment, the sample was grounded using silicon carbide

abrasive papers down to 1,000 grit, degreased in acetone and then ethanol and dried in air.

A PAR2273 Electrochemical Measurement System manufactured by EG&G was used for all electrochemical measurements. In the potentiodynamic polarization measurements, the scan rate was 0.166 mV/s. In the potentiostatic polarization experiments, the samples were polarized at 0 V/SCE for 15 min. Prior to the Mott-Schottky measurements, the electrodes were polarized at designated potentials for 15 min so that a stable passive film could form on the electrode surfaces. The potential was applied by successive displacements of 20 mV from -200 to 600 mV. A perturbing sinusoidal potential was superimposed with amplitude of 10 mV. The testing frequency was 1,000 Hz (Liu *et al.*, 2007). Each type of electrochemical measurement was repeated at least three times.

2.3 X-ray photoelectron spectroscopy measurements

X-ray photoelectron spectroscopy (XPS) analysis was performed *ex situ* on the samples after immersion in the CH and CH-CN solutions for 60 min at open-circuit potential. The O1s, C1s and Ca2p core-level spectra and the core-level spectra of all elements in alloy were recorded with an ESCALAB250 X-ray photoelectron spectrometer using monochromatic Al Kα (1,486.6 eV) radiation. The binding energy scale was calibrated to give an Au 4f_{7/2} line position at 83.98 eV. The pressure in the analysis chamber was maintained about 2 × 10⁻⁹ Pa, and the bombardment diameter was 500 μm. Peak identification was performed by reference to an XPS database (Moulder *et al.*, 1995). An XPS Peak 41 software package was used for data acquisition and analysis. The atomic ratios were calculated from the photoelectron peak areas. To eliminate the air exposure influence on the surface components of the passive films during the test, the surface components is wiped off.

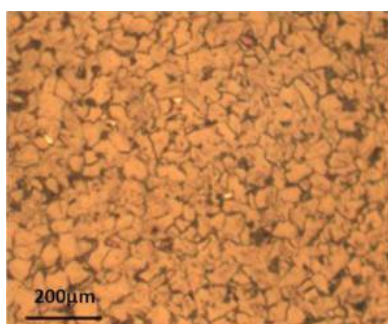
2.4 Atomic force microscopy

The surface morphologies of the passive films analysis were studied after immersion in the CH and CH-CN solutions for 60 min at open-circuit potential. It was characterized by atomic force microscopy (AFM, CSPM5500) with tapping AFM. The scan frequency is 1 Hz, and the scan area is 1,168 × 1,168 nm.

Table I Composition of the rebar (mass%)

Sample	C	Si	S	P	Mn	Fe
Rebar	0.16	0.17	0.034	0.035	0.50	99.101

Figure 1 The metallographic phase of the rebar

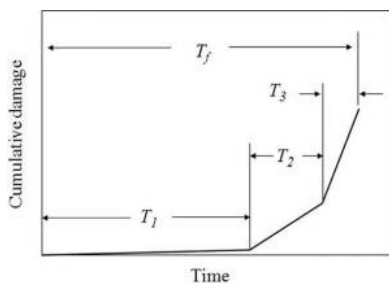


3. Results and discussion

3.1 The influence on the resistance of the pitting corrosion

Corrosion-induced deterioration of reinforced concrete can be modeled in terms of three component steps (Wang and Li, 1999), time for the pitting corrosion initiation (T_1); time, subsequent to corrosion initiation, for appearance of a crack on the external concrete surface (T_2); and time for surface cracks to progress into further damage and develop into spalls (T_3), to the point where the durability service life (T_f) is reached. Figure 2 shows the schematic plot of cumulative damage versus time. The time for pitting corrosion initiation (T_1) is about 80 per cent of the total durability service life (T_f). Therefore, it is crucial to prolong the time of pitting corrosion initiation (T_1) for prolonging the total durability service life.

Figure 2 The schematic plot of cumulative damage versus time



For the concrete structures, especially the marine concrete structures, the chloride ions could cause breakage of the passive films, leading to pitting corrosion of rebar. It is a major reason to decrease the life time of the concrete structure. Figure 3 shows the critical chloride ion concentration of the pitting corrosion of the rebar in the CH and CH-CN solutions. In Figure 3, the passive films are not broken, while the chloride ion concentration is lower than 0.05 mol/L in the CH solution. The corrosion current density increases dramatically because of oxygen evolution reaction, according to the Pourbaix diagram of Fe-H₂O (Cao, 2008). However, the pitting corrosion takes place when the chloride ion concentration is increased to 0.06 mol/L. The results imply that the chloride ion concentration of the pitting corrosion of the rebar is between 0.05 and 0.06 mol/L in CH solution. A similar analysis (Figures 4 and 3) shows that the critical chloride ion concentration of the pitting corrosion of the rebar is between 0.18 and 0.20 mol/L in CH-CN solution. Thus, the calcium nitrite addition could increase the critical chloride ion concentration of the pitting corrosion, where it prolongs the service life time of the reinforced concrete constructions.

As we know, the resistance of the pitting corrosion of the materials depends on characteristics of the passive films, such as component (Liu *et al.*, 2007), surface morphology (Walls *et al.*, 1996; Xu *et al.*, 1993), microstructure, electronic structure (Vignal *et al.*, 2002; Zhang and Cheng, 2010; Li *et al.*, 2007; Lin *et al.*, 2005), etc. Therefore, the influence of calcium nitrite on the passive films is investigated from component, surface morphology and electronic structure of the passive films.

Figure 3 The critical chloride ion concentration of pitting corrosion for rebar in the CH solution

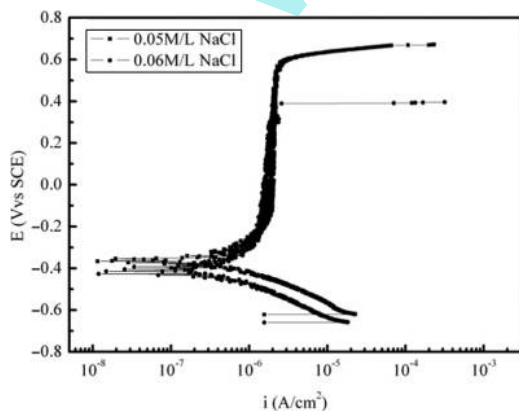
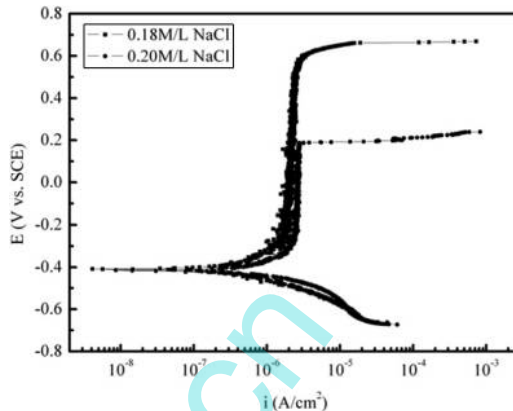


Figure 4 The critical chloride ion concentration of pitting corrosion for rebar in the CH-CN solution



3.2 The influence on components of the passive films

The compositions of the passive films are the main factor for the resistance of the pitting corrosion. XPS analysis was undertaken to provide more information regarding the composition of the passive films. XPS survey spectra, shown in Figure 5, identify Fe, O, Ca and C peaks. The O1s depth profile XPS spectra of the passive films formed in the CH and CH-CN solutions are shown in Figures 6 and 7. The passive films mainly consist of Fe_{ox} and Fe_{hydrox} in both the solutions. It indicates that the calcium nitrite inhibitor does not change the compositions of the passive films. The atomic ratios of Fe_{hydrox} and Fe_{ox} are calculated by O1s depth profile XPS spectra (Figures 6 and 7) of the passive films that were formed in the CH and CH-CN solutions. The calculating results are shown in Figure 8. It could be seen that the atomic ratio of Fe_{hydrox} and Fe_{ox} is about 0.4 near the surface of the passive films formed in the CH solution (about 10 s sputtering time). After 20 s of sputtering time, the ratios are larger than 0.8. However, the atomic ratio of Fe_{hydrox} and Fe_{ox} is about 0.6, as the passive films formed in the CH-CN solution. The content of the Fe_{hydrox} is increased near the surface of the passive films in the CH-CN solution, which is favorable to keep the stabilization of the passive films and improve the repassivation property (Pou *et al.*, 2004). Except for a little

Figure 5 XPS survey spectra for the passive films formed in CH and CH-CN solutions

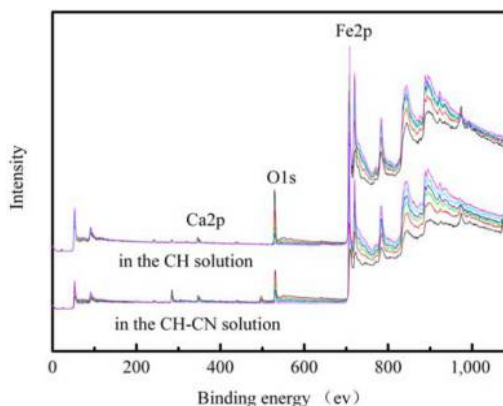


Figure 6 O1s XPS depth profile spectra for the passive films formed in the CH-CN solution

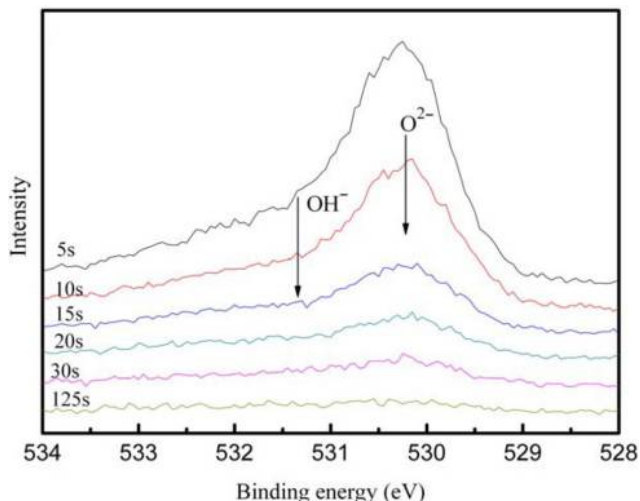


Figure 7 O1s XPS depth profile spectra for the passive films formed in the CH solution

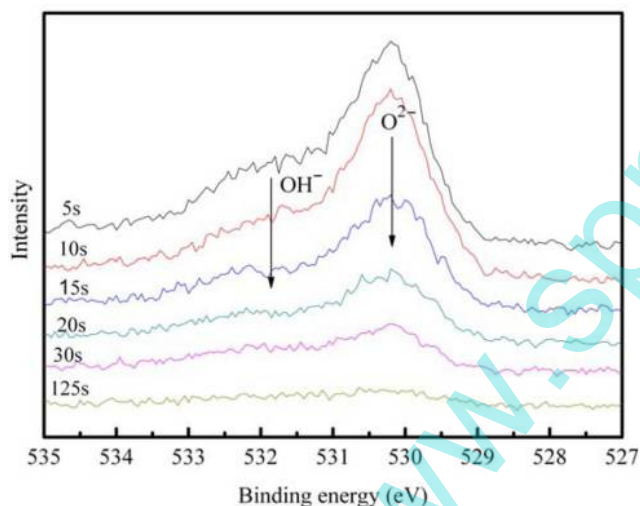
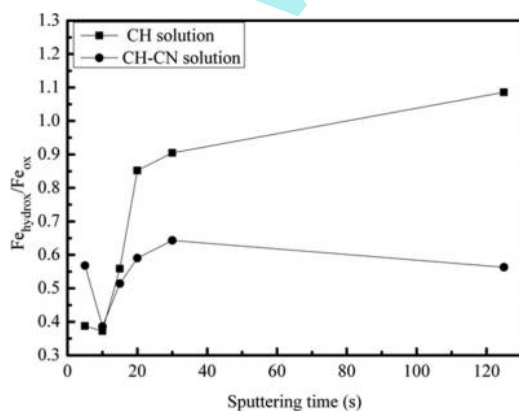


Figure 8 The atomic ratios of $\text{Fe}_{\text{hydrox}}$ and Fe_{ox} of the passive film formed in CH and CH-CN solutions



depth near the surface of the passive films, the ratio of $\text{Fe}_{\text{hydrox}}$ and Fe_{ox} of the passive films formed in the CH-CN solution is lower than that formed in the CH solution. Therefore, the calcium nitrite inhibitor could decrease the ratio of $\text{Fe}_{\text{hydrox}}$ and Fe_{ox} and the $\text{Fe}_{\text{hydrox}}$ content of the whole passive films. Many previous studies have identified that the resistance of the pitting corrosion of the passive films consisting Fe_{ox} is better than those consisting $\text{Fe}_{\text{hydrox}}$ (Pou *et al.*, 2004; Yu *et al.*, 2001). Thus, calcium nitrite could decrease the $\text{Fe}_{\text{hydrox}}$ content of the passive films to improve its resistance of pitting corrosion.

3.3 The influence on surface morphologies of the passive films

The composition could significantly affect the resistance of the pitting corrosion of the passive films. The surface morphologies of the passive films, such as surface roughness, could also dramatically affect its resistance of the pitting corrosion. The pitting corrosion can easily take place on the rough surface of the passive films (Walls *et al.*, 1996). Xu *et al.* (1993) thought that the electric field strength was not uniformly distributed at the films/solution interface. At the films/solution interface, it is larger at the concave than at the flat region. Films at concave sites will breakdown preferentially and become incipient pits when the condition is right. The films rupture and the pitting corrosion takes place. Figures 9 and 9 shows the two- and three-dimensional surface morphologies of the passive films of the rebar formed in the CH and CH-CN solutions. The surface of the passive films formed in the CH solution is rough and has many concave sites (Figure 9), while in the CH-CN solution, the concave sites disappear and the surface of the passive films becomes even (Figure 10). In this work, it shows as similar result as the previous study (Girèienė *et al.*, 2005). The fractal dimensions (D_f) could be used to evaluate and illuminate the roughness of the passive films (Pan *et al.*, 2011). The D_f values are 2.63 and 2.25 for the passive films of the rebar formed in the CH and CH-CN solutions, respectively. Calcium nitrite could make the passive films smooth, which could improve the resistance of the pitting corrosion.

3.4 The influence on electric structure of the passive films

It is well known that there are some relationships between the semiconducting properties and the resistance of pitting corrosion of the passive films. The larger donor or acceptor density could easily break down the passive films (Lin *et al.*, 2005). The pitting corrosion will take place. These properties can be determined by analyzing the curves of capacitance as a function of the electrode potential, which reflects the charge distribution in the passive films. The interfacial capacitance, C , is obtained using the formula $C = -1/\omega Z''$. Assuming that the capacitance of the Helmholtz layer can be neglected, the measured capacitance C is equal to the “space charge” capacitance, C_{sc} (Sikora and Macdonald, 2002). According to the Mott–Schottky theory, the relationship between C_{sc} and E can be expressed as (Sikora and Macdonald, 2002; Carnezin *et al.*, 2005; Belo *et al.*, 1999):

Figure 9 The surface morphologies of the passive film formed in the CH solution

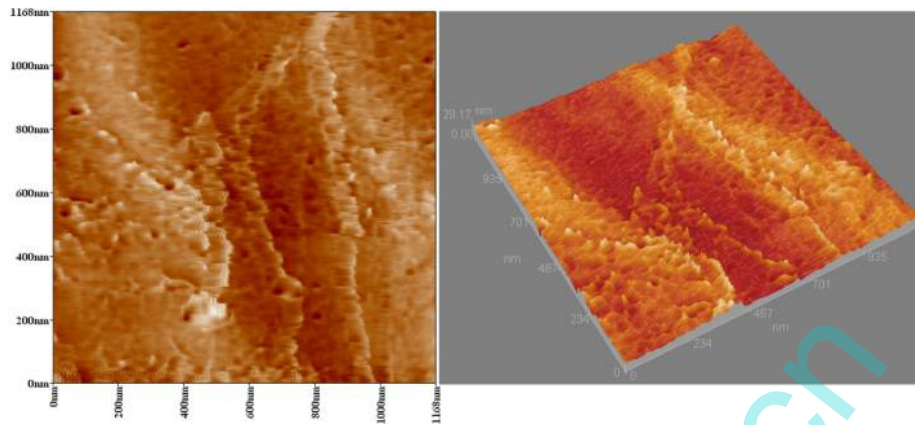
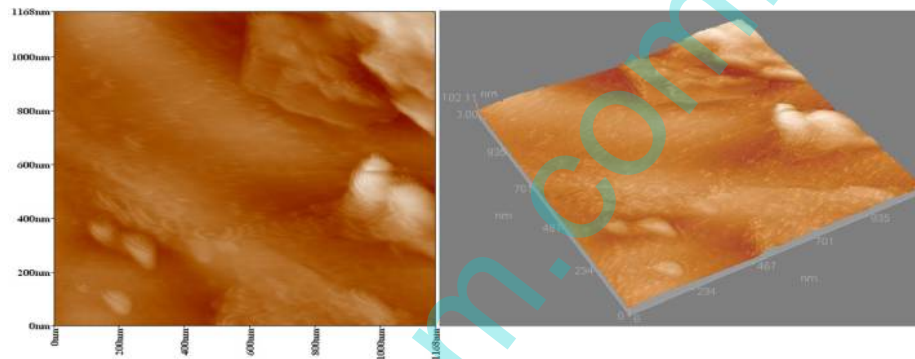


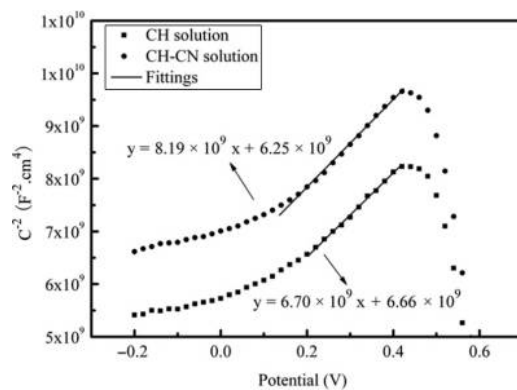
Figure 10 The surface morphologies of the passive film formed in the CH-CN solution



$$\frac{1}{C_{sc}^2} = \frac{2}{\epsilon \epsilon_0 q N_d} \left(E - E_{fb} - \frac{kT}{e} \right) \quad (1)$$

where ϵ_0 is the vacuum permittivity constant (8.85×10^{-14} F cm^{-1}), ϵ is the dielectric constant of the passive films, taken as 12 (Lide, 1995), q is the elementary charge ($+e$ for electrons and $-e$ for holes), N_d is the donor or acceptor density, E_{fb} is the flat band potential, k is Boltzman's constant and T is the absolute temperature. N_d can be determined from the slope of the experimental $1/C_{sc}^2$ vs E plots, while E_{fb} comes from the extrapolation for $1/C_{sc}^2 = 0$. Many studies (Stimming and Schultze, 1979; Delnick and Hackerman, 1979; Azumi *et al.*, 1987; Searson *et al.*, 1988; Wilhelm and Hackerman, 1981; Abrantes and Peter, 1983) have suggested that passive films formed on iron are n-type semiconductive films with a high donor density of 10^{25} - 10^{27} m^{-3} . In Figure 11, Mott-Schottky curves are shown for the passive films formed at the open-circuit potential in CH and CH-CN solutions. The straight lines with positive slope indicate the passive films are n-type semiconductive films. The semiconductive type of the passive films is not changed by the calcium nitrite addition. The donor density (N_d) values of the passive films are 1.76×10^{21} and 1.44×10^{21} cm^{-3} in the CH and CH-CN solutions, respectively. The donor densities (N_d) are decreased when 10 g/L $\text{Ca}(\text{NO}_2)_2$ is added in the CH solution. It is probably due to the decrease in the $\text{Fe}_{\text{hydrox}}$ content in the passive films when calcium nitrite is added to the CH solution (Ahn and Kwon, 2004).

Figure 11 Mott-Schottky plots of the passive film formed in CH and CH-CN solutions



According to equation (1), the plat potential (E_{fb}) of the passive films could be calculated, and the values are -0.76 and -0.99 V in the CH and CH-CN solutions, respectively. The E_{fb} could be expressed by Nerstian Equation (Delnick and Hackerman, 1979; Azumi *et al.*, 1987) as follows:

$$E_{fb} = -E_0^f/q + \Delta\Phi_H, \quad (2)$$

where E_0^f/q is the potential drop of the space charge layer and $\Delta\Phi_H$ is the potential difference between electrode surface and outer Helmholtz layer. The electrode surface

potential is determined by the surface charge. The potential drop of the space charge layer equals to zero at the plat potential in semiconductor electrode. Therefore, the variation of the plat potential reflects the variation of the Helmholtz double layer potential (Stimming and Schultze, 1979). Anion absorption on the surface of the passive films could arouse the negative charge values on the surface, which would cause a decrease in $\Delta\Phi_H$. Therefore, the plat potential would shift negatively (Lin *et al.*, 2005). The more the anions absorb on the surface of the passive films, the more negative is the plat potential. It means that anions, such as chloride ions, absorb on the passive films that formed in the CH-CN solution hardly.

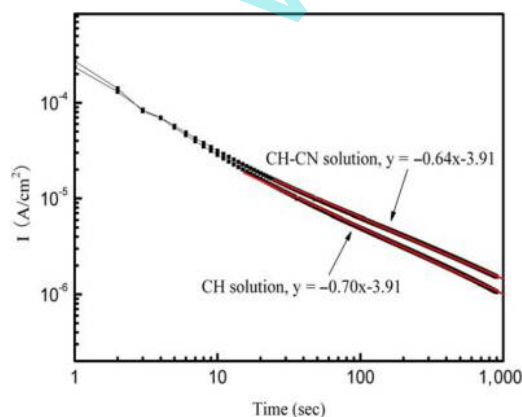
3.5 The influence on compactness of the passive films

The compact property will influence the electrolyte transportation in the passive films and then affect the corrosion resistance property. The variations of current with time for the different specimens were measured at a fixed potential (0 V). If the contribution of the double layer charge is neglected, the initial fall of current density should be related to film growth on the electrode surface. Under potentiostatic conditions, the current I of many time-dependent processes well described by the “universal law” (Lohrengel, 1993). The current decreased with time according to the relationship below (Hassan, 2005):

$$I = 10^{-(A+k\lg t)}, \quad (3)$$

where k represents the slope of the double-log plot for potentiostatic polarization. According to Gebert *et al.* (2001) and Galvele *et al.* (1990), $k = -1$ indicates the formation of a compact, high field-controlled, highly protective oxide layer, while $k = -0.5$ indicates the presence of a porous and diffusion-controlled oxide layer. Figure 12 shows the double-log plots of current-time for the rebar at 0 V in the CH and CH-CN solutions. The values of $k = -0.70$ and -0.64 are obtained for the formation of the passive films in CH and CH-CN solutions, respectively. It implies that the passive films formed in both the solutions are loose and porous. The compactness of the passive films is not changed by calcium nitrite addition.

Figure 12 Double-log plots of current-time for rebar in CH and CH-CN solutions



4. Conclusions

The 10 g/L calcium nitrite addition did not change the properties of the passive films formed on the surface of rebar in the CH solution, such as compactness and semiconductor type (n-type). However, it decreased the donor density (N_d) and the content of Fe_{hydrox} in the passive films, smoothed the films surface and increased the plat potential. These all are benefits for improving the resistance of pitting corrosion.

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