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Electrochemical study on semiconductive properties of the passive film on rebar in concrete*

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Abstract: The electrochemical behavior of metallic passive film on rebar in concrete is characterized by its semiconductive nature. The charge distribution at the interface between a semiconductor and an electrolyte is often determined by measuring the capacitance of the space-charge layer (C_{SC}) as a function of the electrode potential (E). When the space charge-layer serves as the depletion layer, the relation of C_{SC}^{-2} vs E resembles a Mott-Schottky plot (M-S plot). The semiconductive properties of the passive film on rebar in concrete were analyzed with M-S plots to study the effect of chloride ions and mineral admixtures on rebar passive films. Some rebar electrodes were immersed in simulated concrete pore solutions, while others were embedded in concrete with/without mineral admixtures. In saturated $\mathrm{Ca(OH)_2}$ solutions, the relation of C_{SC}^{-2}-E of rebar electrodes shows linear Mott-Schottky relationship indicating that the passive film on rebar is a highly disordered n-type semiconductor, with donor density (N_{D}) in the order of 10^{26} m^{-3}. After adding chloride ions (Cl^{-} wt%<0.2%) in system solutions, the M-S plot slopes significantly decreased and N_{D} increased, suggesting that chloride ion will cause passive film corrosion and breakdown. The M-S plots of the passive film on rebar electrodes embedded in concrete were similar to those immersed in simulated system solution. However, N_{D} of those in concrete with mineral admixtures tended to be a little smaller, indicating that introducing proper quantity admixtures into concrete could make the rebar passive film have a thicker space-charge layer and therefore a thicker passive film layer.

Key words: Mott-Schottky (M-S) Plot, Rebar electrode, Passive film, Simulated concrete pore solution, Mineral admixture
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INTRODUCTION

Steel rebar embedded in concrete is protected against corrosion by the thin passive film on its surface and the physical protection from concrete. The alkaline environment (pH≥12.5) of the concrete pore solution triggers passivation on the rebar surface and formation of the protective oxide film. The physical protection of concrete coverage hinders the invasion of aggressive agents. However, this passivity can be broken down by local pH loss as a result of concrete cracking or the electrolyte reacting with the environment. On the other hand, aggressive agents such as chlorides may penetrate the concrete and initiate corrosion of the rebar.

During the last decades, rebar corrosion has been the subject of numerous researches mostly focused on passive films, in order to gain comprehensive understanding of the growth mechanisms, structure and composition of the films. However, there are difficulties in experimental measurements of reinforced concrete samples, including the electrode and cell designs (e.g. the position of the reference and counter electrode), the large potential drop (IR) in concrete and its compensation, the development of macro-corrosion cells, the restriction of oxygen diffusion, etc. An alternative approach (Veleva *et al*., 2002) is to use

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electrodes immersed in appropriate solutions to simulate the concrete pore solution environment. Because simulated concrete pore solutions allow researchers to obtain comparative results and to control some parameters that are difficult to manage in reinforced concrete samples, they have been widely utilized to investigate the properties of passive film on rebar (Veleva *et al.*, 2002; Saremi and Mahallati, 2002; Moreno *et al.*, 2004; Wang *et al.*, 1998a; 1998b; Du *et al.*, 2001; Hu *et al.*, 2003).

Many surface physics and electrochemistry techniques such as Moessbauer spectroscopy, surface enhancement Raman spectroscopy (SERS), X-ray photoelectron spectroscopy (XPS), electrochemical impedance spectroscopy (EIS) and electrochemical noise (EN) are widely used to study the passive films on rebar. Mott-Schottky (M-S) analysis is a powerful tool to probe the semiconductive properties of passive films on metals, by which the thickness of space-charge layer, donor or acceptor density and flat-band potential for the passive film can be obtained. M-S analysis has been successfully employed to investigate the surface of many metals such as copper (Knauth and Massiani, 1998), stainless steel (Veleva *et al.*, 2002; Ge *et al.*, 2003) and carbon steel in various electrolytes. So far, for carbon steel or iron, the solutions used as electrolytes were usually borate (Ge *et al.*, 2003; Li *et al.*, 2002; Cheng *et al.*, 2002), chromate (Cheng and Luo, 1999; 2000), and bicarbonate (Baek *et al.*, 2001). There is little information on semiconductive properties of passive films on rebar in alkaline media, and especially in concrete extract solution. Passivation of Fe is a relatively complex process not completely understood yet.

Utilizing the M-S analysis method, this research is aimed at preliminarily studying the electronic properties of passive films on rebar in simulated concrete pore solutions and embedded in concrete, as well as the effect of chloride ions and mineral admixtures in concrete on rebar passive films.

EXPERIMENTAL PROCEDURE

Electrodes and solutions

Rebar specimens of Φ10 mm×5 mm were cut from architectural plain steel rods, Q235. The chemical composition of the steel was (in wt%): 0.09 C, 0.36 Mn, 0.22 Si, 0.03 S, 0.032 P, with the balance being Fe. Electrodes were prepared by attaching a copper wire to its rear and covering all faces except the working face with epoxy resin. The exposed faces were sanded with 1000 grit silicon carbide papers, and rinsed by acetone and de-ionized water prior to testing. Some of these electrodes were immersed in system solutions for measurement while others were embedded in the center of Φ3 mm×4 mm concrete cylinders, with the working faces extending downward to one end of the concrete cylinder and a copper wire leading out of the other end. The composition of the concrete (with various admixtures) was Cement:Water:Sand=1:0.6:3. The mineral admixtures to concrete were blast furnace slag, fly ash, high performance marine concrete admixture, and silica fume, respectively. The concrete samples were wet-cured at ambient temperature, and moved to saturated $Ca(OH)_2$ solution before M-S measurement of the rebar electrodes in concrete at age of 3 d.

All solutions were made from analytical-grade reagents and de-ionized water. Chloride ion was added in the form of NaCl. Saturated $Ca(OH)_2$ solution was used as simulated concrete pore solution with pH of 12.5 at 25 °C. Chloride ions with different concentration were added as aggressive ions to this base solution. The M-S plot measurements were acquired by a CHI 660a Electrochemical Workstation at 1000 Hz in the potential range 0.6~−1.0 V, with a perturbing signal of 5 mV. During the experiment, platinum electrode was used as counter electrode, and saturated calomel electrode (SCE) as the reference electrode which was connected to the working electrode with a salt bridge. All the potential values in this paper are relative to the SCE. All tests were carried out at ambient temperature.

Analysis of M-S plots

The passive films of many metals exhibit electrochemical properties of a semiconductor. When a semiconductor contacts a solution containing redox couples, charges are transferred between the semiconductor phase and the solution phase. When static balance is reached, the semiconductor phase and the solution phase bear opposite charges. The surplus charges of the semiconductor phase are distributed in the space charge-layer. The charge distribution at the interface between a semiconductor and an electrolyte is often determined by measuring the capacitance of the space charge-layer (C_{SC}) as a function of the electrode potential (E). When the space-charge layer serves as a depletion layer, the relation of the capacitance and the potential conforms to the Mott-Schottky equation (Morrison, 1981; Sukhotin *et al.*, 1989):

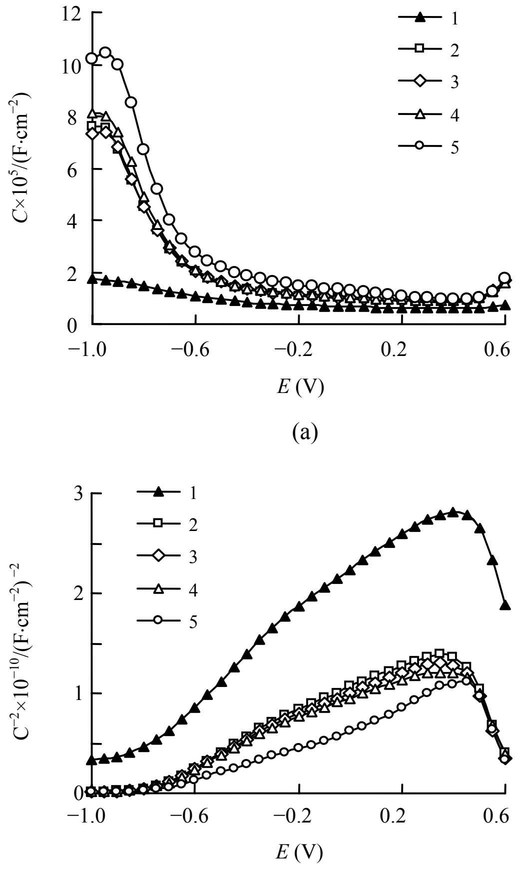
$$\frac{1}{C_{SC}^2}=\frac{2}{\varepsilon\varepsilon_0 qN}\left(E-E_{fb}-\frac{kT}{q}\right). \tag{1}$$

The M-S relationship ($1/C_{SC}^2$ vs E plot) expresses the potential dependence of C_{SC} of a semiconductor electrode under depletion conditions, where N represents the donor (N_D) or acceptor density (N_A), ε is the dielectric constant of the passive film, ε_0 is the vacuum permittivity (8.85×10^{-14} F/cm), q is electron charge ($+e$ for electron, $-e$ for vacancy, $e=1.602\times10^{-19}$ C), E_{fb} is the flat band potential, k is the Boltzmann constant (k=1.38×10^{-23} J/K) and T is the absolute temperature (kT/q is only about 25 mV at the ambient temperature and is assumed to be negligible). N_D and N_A 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.

RESULTS AND ANALYSIS

Semiconductive properties of passive films on rebar in simulated concrete pore solution

It has been suggested that the passive film on iron consists of an inner layer of Fe_3O_4 and an outer layer of γ-Fe_2O_3 (Veleva *et al.*, 2002; Wang *et al.*, 1998a; 1998b; Li and Luo, 1999). Usually, the outer layer is in the range of 1~4 nm, and the inner layer may be thinner (<1 nm). Therefore, the properties of a passive film depend on the thicker outer layer of γ-Fe_2O_3. The rebar electrode was placed in saturated $Ca(OH)_2$ solution and the capacitance was measured after one hour of immersion. The corresponding M-S plot (C^{-2} vs E plot) is shown as Curve 1 in Fig.1b. The slope of the M-S plot from −0.78 V to 0.37 V is positive, resembling the properties of n-type semiconductors.



(a)

(b)

Fig.1 Capacitance and Potential curves and M-S plots of rebar electrode in saturated $Ca(OH)_2$ for 1 h then adding Cl^- for 1 h. (a) Capacitance vs Potential curves; (b) M-S plots

Cl^- concentration (wt%): 1: 0.0%; 2: 0.02%; 3: 0.05%; 4: 0.1%; 5: 0.2%

In the section near flat-band potential, −0.875 V, the capacitance values are pretty high (Fig.1a), which is attributed to the Helmholtz layer. Due to the chemical complexity of the system, the M-S relation is not absolutely linear. There are two linear sections (from −0.78 to −0.27 V and from −0.27 to 0.37 V) in the M-S plots. Thus, the passive films contained two levels of donors, a shallow one and a deep one, in the space charge layers. Previous studies revealed that Fe_3O_4 and γ-Fe_2O_3 in a passive film have an inversed spinel structure (Cai *et al.*, 2003). In Fe_3O_4, one-third of the positions of the iron ions are tetrahedral positions occupied by Fe^{3+}, and two-thirds are octahedral positions occupied equally by Fe^{3+} and Fe^{2+}. In γ-Fe_2O_3, one-ninth of the octahedral positions are vacant, and all iron is in the trivalent state. The donors in the passive film on iron are attributed to Fe^{2+} ions from Fe_2O_3. The shallow donors work on the substitution of Fe^{3+} ions by Fe^{2+} on the tetrahedral positions of Fe_2O_3 and the deep donors do the same substitution on the octahedral positions (Hakiki *et al.*, 1998). When the potential is in the range of −0.78~−0.27 V, the slope of the M-S plot is attributed to the shallow donor. And when the potential is in the range of −0.27~0.37 V, the ionization of the deep donor causes the donor density to increase and the slope of the M-S plot to decrease (Dean and Stimming, 1987).

Donor densities of the passive film were calculated by Eq.(1), where ε, the dielectric constant of the passive film, is set to 12 (Dean and Stimming, 1987). They are in the order of 10^{26} m^{-3} (Table 1). Thus, the passive film formed by saturated $Ca(OH)_2$ solution is very disordered and conductive. However, this set of donor density is lower than those of the iron passive films in chromate solutions and those in non-oxidant solutions by anodic oxidation, which are in the order of 10^{27} and 10^{28} m^{-3} respectively (Li and Luo, 1999; Dean and Stimming, 1989).

Table 1 N_D (shallow donor) for passive films on rebar in saturated $Ca(OH)_2$ solution

Chloride ion concentration (%)	0	0.02	0.05	0.1	0.2
N_D ($\times10^{26}$ m^{-3})	3.820	7.930	8.283	8.608	13.523
E_{fb} (V)	−0.875	−0.775	−0.775	−0.775	−0.750

Influence of chloride on semiconductor characteristics of passive film on rebar

Curves 2~5 in Fig.1b are the M-S plots of rebar electrode in system solution, in the presence of chloride for one hour after having been immersed in base solution for one hour. The Cl^- ion concentration was 0.02%, 0.05%, 0.1%, and 0.2% respectively. It seems that the essential characteristics of M-S plots of passive films formed in various solutions containing chloride (Cl^-<0.2%) have no change when compared with Curve 1. The passive films in system solution still belong to n-type semiconductor. Their flat-band potential of the film in the solutions with chloride were similar to that in the reference solution. However, the slopes of M-S plots changed significantly with the increase of chloride. Therefore, the surface charge of the films changed when chloride was added to the solution. The donor densities at different Cl^- levels are shown in Table 1. The results indicate donor densities of passive films on rebar electrode in system solutions rise when Cl^- ion concentration increases, which leads to increasing electric-conductivity of Fe-oxides on films and decreased corrosion resistance of the passive films.

The linearity in the M-S plots is due to the fact that the thickness of a passive film increases linearly with the applied potential. The linear part of the M-S plots at high potential reflects a uniform donor density close to the metal/film interface. The thickness δ_{SC} of the space-charger layer can be calculated by Eq.(2) for n-type semiconductor:

$$\delta_{SC}=\left[\frac{2\varepsilon\varepsilon_0}{eN_D}\left(E-E_{fb}-\frac{kT}{e}\right)\right]^{1/2}. \qquad (2)$$

From Table 1 and Eq.(2), it is clear that the presence of Cl^- ion leads to higher donor density and a decrease in space charge-layer thickness, and consequently makes the passive film thinner and much easier to break down. When chloride ions penetrating concrete cover reach the rebar surface, they are absorbed at defective spots of the film, leading to increased N_D by the doping function of Cl^- ion. If the concentration of Cl^- ion is high enough, oxygen and oxyhydrogen ions will be replaced on the film surface. As a result, the passive film on rebar will be difficult to form or its growth will be inhibited.

Effect of mineral admixtures in concrete on semiconductor characteristics of passive films on rebar

M-S plots of rebar electrodes embedded in concrete with various mineral admixtures at 3 d are illustrated in Fig.2. Compared with those immersed in simulated concrete pore solutions, there are no evident changes in the semiconductive properties of the passive film on rebar electrodes. Their flat-band potential has shifted a little bit, to about −0.9 V.

However, the slopes of the M-S plots changed more substantially. The slopes of the M-S plots of the rebar passive films formed in concrete with admixtures are significantly larger than those acquired in control specimen (Curve 1). Similarly, we can learn from Eqs.(1) and (2) that the larger the M-S plot slope, the smaller the donor density N_D (Table 2), the thicker the space-charger layer and consequently, the thicker

Table 2 N_D **(shallow donor) for passive films on rebar embedded in concrete with various admixtures**

Concrete admixture	No admixture	Blast furnace slag	Fly ash	Marine concrete admixture	Silica fume
wt%	0	30	30	30	10
N_D ($\times 10^{26}$ m^{-3})	2.327	1.353	1.664	1.547	1.760

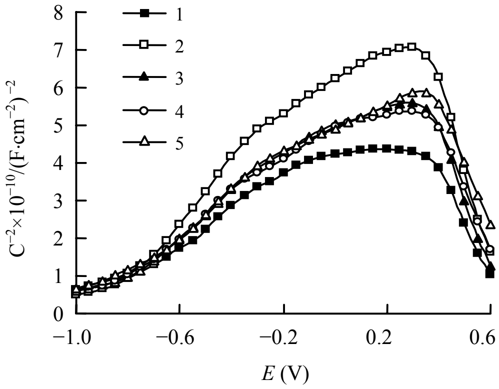


Fig.2 M-S plots of rebar electrodes embedded in concrete at 3 d with different admixtures
1: Reference sample; 2: Furnace slag 30%; 3: Fly ash 30%; 4: Marine admixture 30%; 5: Silica fume 10%

the passive film layer. Therefore, the chances of passive film breakdown and pitting initiation on the rebar embedded in concrete with admixtures are reduced.

This beneficial characteristic is explained below. Mineral admixtures are added as fine granulates and react with calcium hydroxide, producing cementitious products, which leads to improved distribution of pore size and pore shape of concrete (Yang and Wang, 2004), increased concrete resistivity, reduced permeability and diffusivity of chloride and other corrosive species through the concrete (Zemajtis, 1998; Montemor *et al.*, 2002; Yang and Wang, 2004) and therefore reduced corrosion current density (Tuerkmen and Gavgalı, 2003; Tuerkmen *et al.*, 2003). It was discovered that the presence of fly ash in concrete affects the composition and thickness of the passive film on steel (Montemor *et al.*, 2000). Based on our research and previous studies, it is concluded that mineral admixtures in concrete can stabilize the passive film on rebar and decrease the initiation of corrosion. However, it is more complicated to analyze the semiconductive behavior of the rebar electrodes embedded in concrete than of those in simulated system solutions due to the complexity of a concrete protection layer and its actual concrete pore solution. The structure and electric properties of the passive film on rebar embedded in concrete need further detailed research.

CONCLUSION

(1) The passive film on rebar in concrete is a highly disordered n-type semiconductor with the donor density N_D in the order of 10^{26} m^{-3} and flat-band potential of about −0.85 V.

(2) In the presence of Cl$^-$ ion (wt%<0.2%) in simulated concrete pore solutions, the slope of M-S plots decreases and N_D increases, which causes decreased corrosion resistance and a thinner passive film on rebar. Consequently, the passive film tends to be more susceptible to breakage.

(3) The application of proper quantity mineral admixtures in concrete could make the rebar passive film have a thicker space-charger layer and therefore a thicker passive film layer, which can inhibit film breakdown and delay pitting initiation on rebar.

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