

## The Effects of Deformation on Corrosion Behavior of Stainless Steel in Chlorides Contaminated Concrete Pore Solution

Xingguo Feng<sup>1,\*</sup>, Xiangyu Lu<sup>2</sup>, Longqia Guo<sup>1</sup>, Da Chen<sup>1,\*</sup>

<sup>1</sup> Jiangsu Key Laboratory of Coast Ocean Resources Development and Environment Security, Hohai University, Nanjing 210098, Jiangsu, China

<sup>2</sup> School of Materials Science and Engineering, Jiangsu University of Science and Technology, Zhenjiang 212003, Jiangsu, China

\*E-mail: [chenda@hhu.edu.cn](mailto:chenda@hhu.edu.cn)

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The effect of deformation on corrosion behavior AISI 304 stainless steel in a simulated carbonated concrete pore solution was studied by open circuit potential, electrochemical impedance spectra, Mott-Schottky, and potential step tests. The results suggest that the values open circuit potential and impedance significantly decreased with the increasing deformation. The passive films are heavy doped, and the space-charge layer becomes thinner when the magnitude of deformation increased. The activity of stainless steel also obviously increases with the degree of deformation. In addition, the synergistic effect of deformation and aggressive ions (Cl<sup>-</sup>) on the degradation of passive film in the carbonated pore solution is confirmed.

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**Keywords:** Concrete, stainless steel, corrosion; EIS; Mott-Schottky

### 1. INTRODUCTION

Stainless steel reinforcing bar is one of the reliable solutions to guarantee the durability of concrete structures in extremely aggressive environments [1]. An earlier study reported that a concrete pier constructed with stainless steel bars exposed to a tropical marine environment still shows good performance after working 60 years [2]. For estimating the service life of stainless steel concrete structure, many researchers studied the corrosion behavior of stainless steel in concrete environment. Fajardo [1] compared the corrosion behavior of a low-nickel stainless steel and AISI 304 stainless steel in a carbonated pore solution with different concentrations of Cl<sup>-</sup>. The results show that the pitting potential of stainless steels significantly decreased with the increasing concentrations of Cl<sup>-</sup>. Moreover, the two stainless steels exhibited similar corrosion character in the carbonated pore solution. Freire [3]

studied the corrosion behavior of AISI 304 stainless steel in the simulated pore solutions with different pH values and found that pitting potential significantly increases when the pH increase from 9 to 13. Furthermore, the results also suggest that the resistance of passive film obviously decreases as the pH drop from 13 to 9 in the chlorides contained pore solution. Deus [4] studied the effect of temperature on corrosion potential of stainless steel rebars in concrete and notice that the corrosion potential mirrored the temperature variations. The authors attribute this situation to the temperature induced changes in the chemistry of the passive layer. Elsener [5] studied the Nickel-free manganese bearing stainless steel in the simulated pore solution. The results indicated that the content of chromium oxyhydroxides and Mo(VI) increase, while that of iron(II)oxide decrease when the immersion time prolonged.

The studies about stainless steel reinforcing rebar mainly focus on the effect of environmental factors [1, 3-5] on the corrosion behavior. Actually, the concrete structure always suffered various kinds of strain or stress in engineering. In this present study, the corrosion behavior of tensile stressed AISI 304 stainless steel in carbonated pore solution with different concentration of Cl<sup>-</sup> was studied. The results show that the passive films on the deformed stainless steel are heavy doped. The activity of stainless steel also significantly increases with the magnitude of deformation.

## 2. MATERIALS AND EXPERIMENTS

### 2.1 Materials

The traditional austenitic stainless steels AISI 304 was used in this study. The chemical composition and mechanical property of the studied stainless steel are same to that listed in the previous reference [6]. Samples of the size shown in Figure.1 were adopted for tensile testing. The stainless steel samples were ground using a series of emery papers down to grade 600. Thereafter, the samples were degreased with acetone and covered with a coating of silica gel, leaving an exposed area of 1 cm<sup>2</sup> in the middle. The cement extracts solution was prepared by adding 1000 g ordinary Portland cement (P.O 42.5) to 5 L. The liquid was stirred for 30 min and kept for 4 h, then was filtered [7, 8]. The filtered liquid, with a pH of 12.5, was used as pore solution. To simulate the carbonated concrete pore solution, the cement extracts solution was adjusted to a pH of 9 by a dilute nitric acid solution. Different concentrations of NaCl (0 mol/L, 0.05 mol/L, 0.5 mol/L) were adopted to study the effects of aggressive ions on corrosion behavior of stainless steel.

### 2.2 Experiments

Different deformations, including 0%, 0.4%, 0.8%, 2.0%, 5.0%, 10%, 20% and 40%, were conducted with a home-made tensile machine to study the influence of the degree of strain on the corrosion behavior of samples. The electrochemical experiments were performed by using a CS350 workstation (Corrtest Instrument, China) at room temperature with a classical three-electrode cell. A saturated calomel electrode (SCE) and a platinum plate are used as reference electrode and counter

electrode, respectively. Each electrochemical testing was carried out in triplicate with a new sample each time.

The stainless steel samples are initially reduced potentiostatically at  $-1.0\text{ V}$  for 5 min to remove the oxide film formed by aerial oxidation before experiments [9]. The open circuit potential (OCP) and electrochemical impedance spectra (EIS) of each sample were measured 2 h after the deformations were applied. For EIS measurement, the sweeping frequency is from 11520Hz to 10 mHz with an AC perturbation of 10 mV. After immersing 2 h in pore solution, Mott-Schottky plots were measured from  $-1.5$  to  $1.5\text{ V}$  with a potential step of 50 mV at a frequency of 1000 Hz. The sample was immersed in the solution at OCP for 2 h, then the potential was stepped suddenly up from  $-1.0$  to  $0.5\text{ V}$  and the current was recorded against time.

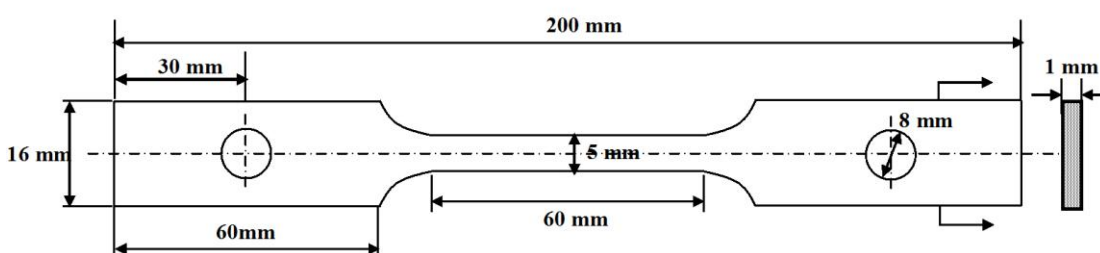


Figure 1. Geometry of specimens used in tensile state.

### 3. RESULTS AND DISCUSSION

#### 3.1 OCP

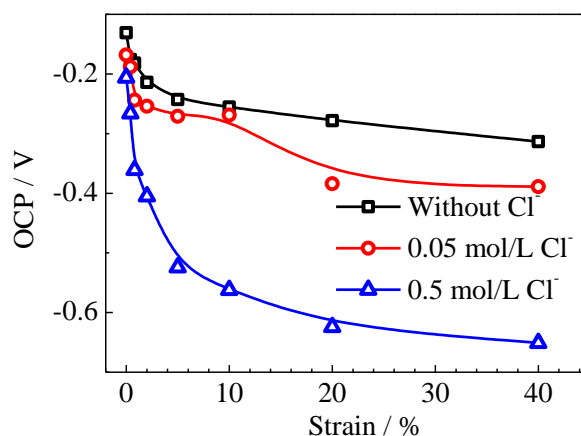


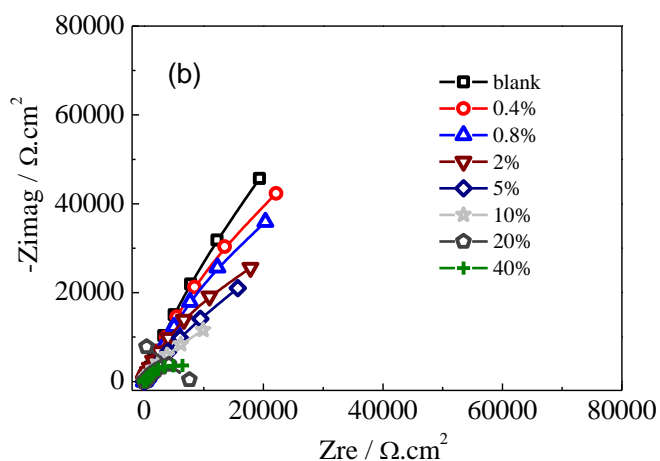
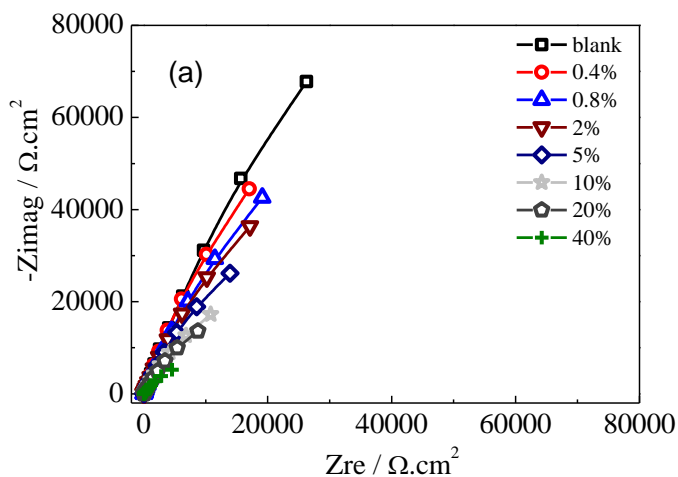
Figure 2. The OCP of samples under different deformation in the carbonated concrete pore solution (pH=9) with various concentrations of  $\text{Cl}^-$ .

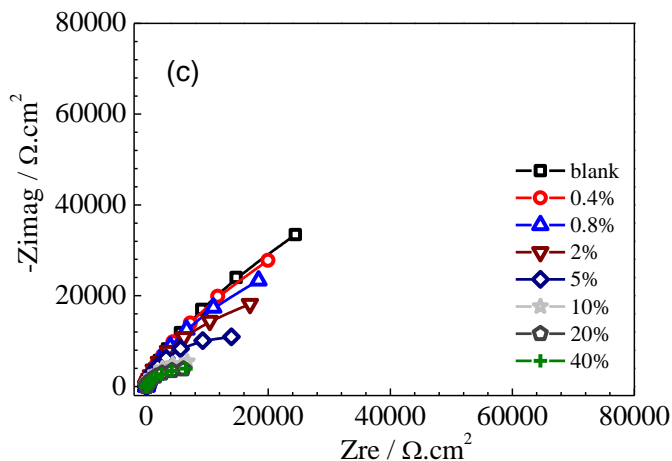
After immersed in pore solution for 2 h, the OCP of the deformed stainless steel is tested and the results are presented in Figure. 2. As the results show, the values of OCP decreased with the

increasing deformation in each solution. In addition, the decrease trend of OCP is more obvious for the samples in the solution with higher Cl<sup>-</sup> concentration. On the other hand, it is easy to notice that the stainless steel samples in solution with higher Cl<sup>-</sup> concentration shows lower OCP values. As many earlier studies [6, 10] reported, the low OCP means the high activity of substrate. Thus, the OCP results suggest that the activity of stainless steel increased with increasing deformation and Cl<sup>-</sup> concentration.

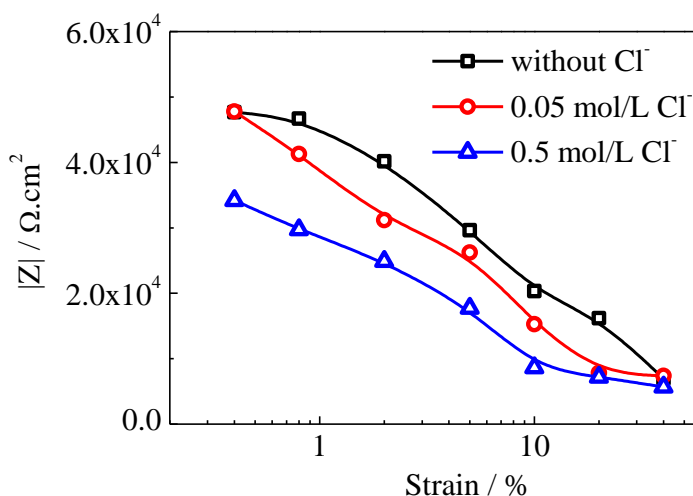
### 3.2 EIS

The Nyquist plots of stainless steel in the carbonated concrete pore solution subjected to various stresses are presented in Figure. 3. The radius of the capacitive loop decreases significantly with increasing stress magnitude in each Cl<sup>-</sup> concentration solution. On the other hand, the radius of the capacitive loop was also found to be decrease with the concentration of Cl<sup>-</sup>. The impedance values of deformed samples at the lowest frequency (0.01 Hz) are presented in Figure. 4. The results show that the impedances decreased with the increasing deformation and aggressive ions (Cl<sup>-</sup>), which together with the OCP results suggest that the activity of stainless steel increasing with the degree of deformation and the concentration of Cl<sup>-</sup>.



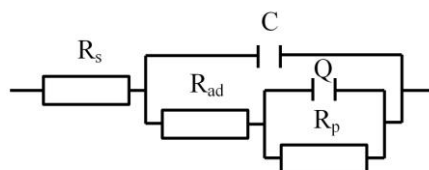


**Figure 3.** Nyquist plots of samples suffering different deformation in carbonated concrete pore solutions (pH=9), (a) without Cl<sup>-</sup>, (b) 0.05 mol/L Cl<sup>-</sup>, (c) 0.5 mol/L Cl<sup>-</sup>.



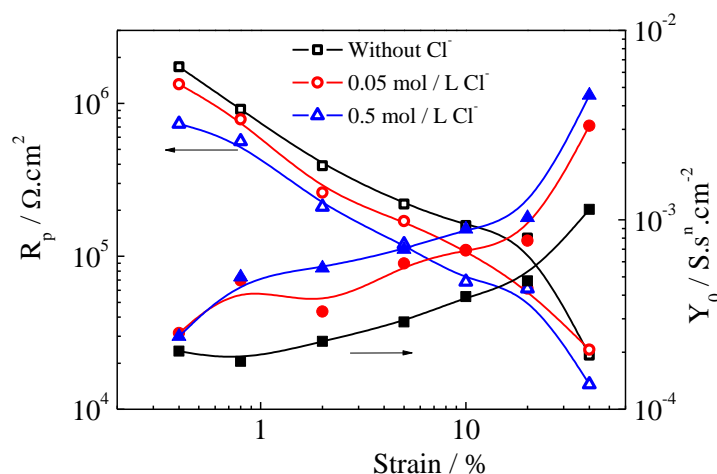
**Figure 4.**  $|Z|_{0.01\text{Hz}}$  of deformed samples in carbonated concrete pore solution (pH=9).

The EIS results are fitted to an equivalent circuit (Figure. 5) by using the Zsimpwin software [11, 12];  $R_s$  represents solution resistance;  $R_{ad}$  and  $C$  represent the resistance and capacitance of the adsorbed layer respectively;  $R_p$  is the polarization resistance of the corrosion process and  $Q$  is the double-layer capacitance.



**Figure 5.** Equivalent electrical circuit for modeling the impedance data.

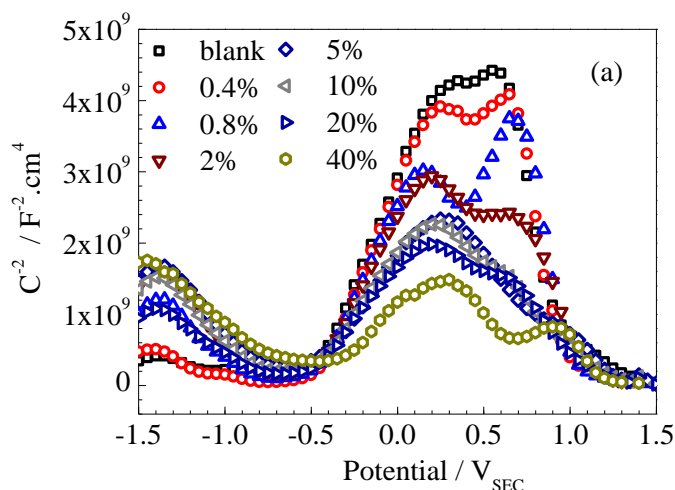
As the results in Figure.6 show, the fitting  $R_p$  results is of the order of magnitude of  $10^5 \sim 10^6 \Omega \cdot \text{cm}^2$ , similar order of magnitude has been reported by Blanco et al [13]. Furthermore, the  $R_p$  significantly decreased with the increasing magnitude of deformation. This situation confirmed that the deformation increased the activity of stainless steel in the carbonated pore solution.

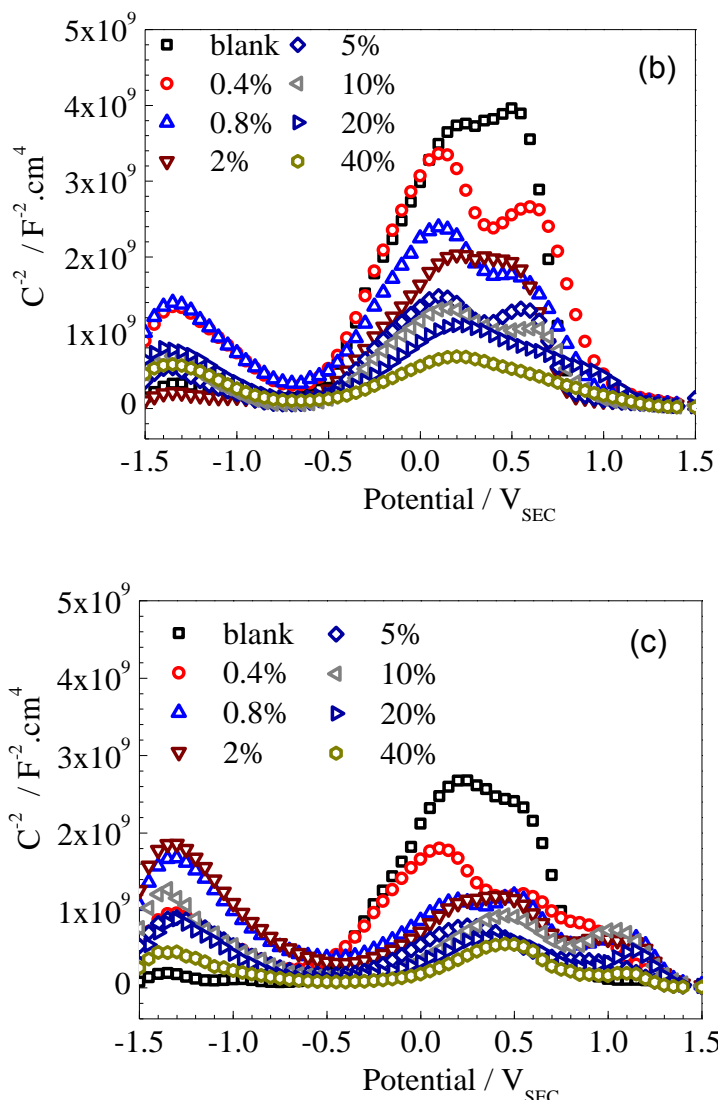


**Figure 6.** The fitting results of  $R_p$  and  $Q$  of deformed samples in carbonated concrete pore solution (pH=9) with different concentration  $\text{Cl}^-$ .

### 3.3 Mott-Schottky

The semi-conductive properties of passive films on stainless steel in the carbonated concrete pore solution are presented in Figure. 7. As the results show, three stages can be observed in the testing potential range. The first stage, with negative slopes, occurred when the potential was below  $-0.7 \text{ V}$ , which suggesting a p-type semiconducting film [14, 15]. Some researchers [16] ascribe this to the capacitance response of a  $\text{Cr}_2\text{O}_3$  layer.





**Figure 7.** Mott-Schottky plots of deformed 304 stainless steel in carbonated concrete pore solutions (pH=9) at a frequency of 1000 Hz, (a) without Cl<sup>-</sup>, (b) 0.05 mol/L Cl<sup>-</sup>, (c) 0.5 mol/L Cl<sup>-</sup>.

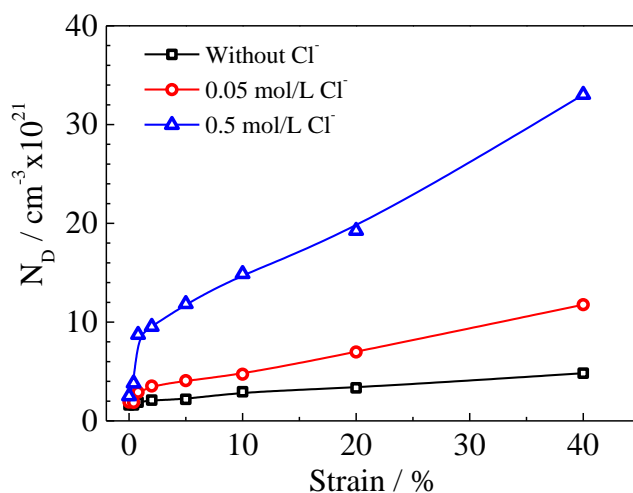
When the potential in the range from -0.7 V to 0.2 V, positive slopes were observed, suggesting an n-type semiconducting film on the surface stainless steel [14, 15]. Hamadou et al [16] thought it is related to the capacitance response of iron oxides. As the potential higher than 0.2 V, negative slopes are observed again, and the situation was attributed to the breakdown of the passive film [17, 18].

Our previous study has demonstrated that the iron oxides film is easy to influence by the deformation and environment factors [6]. Thus, only the semi-conductive properties of the outer iron oxides films are further analyzed in the present study. As the results in Figure.7 show, the values of positive slopes (-0.7 ~ 0.2 V) obviously decreased when the degree of deformation increasing. Based on Mott-Schottky theory [19], the capacitances (C) of n-type semiconductors are given by Eqs. (1)

$$C^{-2} = \frac{2 \left( E - E_{FB} - \frac{kT}{q} \right)}{\epsilon \epsilon_0 q N_D} \quad (1)$$

where  $N_D$  is donor density, which can be concluded from the slope of Mott-Schottky plots.  $\epsilon_0$  is the permittivity of free space ( $8.85 \times 10^{-14}$  F/cm),  $\epsilon$  is the dielectric constant of the passive film ( $\epsilon$  is 15.6 [20]),  $q$  is the electron charge ( $1.602 \times 10^{-19}$  C),  $k$  is the Boltzman constant ( $1.38 \times 10^{-23}$  J/K).  $E_{FB}$  is the flat band potential,  $T$  is the absolute temperature, and  $kT/q$  is negligible as it is only about 25 mV at room temperature [21, 22]. The donor density  $N_D$  is calculated from the slope in Mott-Schottky plots in the range of -0.7 to 0.2 V, and the results are presented in Figure. 8.

As the results in Figure. 8 shows, the donor density is of the order of magnitude  $10^{22}$  cm<sup>-3</sup>, the same order of magnitude has been reported by some other researchers [23, 24]. This situation indicated that the passive film on the 304 stainless steel is highly disordered. The donor densities significantly increased when the magnitude of deformation increasing. Meanwhile, the  $N_D$  also increased with the concentration of Cl<sup>-</sup>. Furthermore, the increment rate of donor density increased with the increasing concentration of Cl<sup>-</sup> and degree of deformation, which suggest that there is a synergistic effect of deformation and aggressive ions (Cl<sup>-</sup>) on the degradation of passive film on stainless steel in the carbonated concrete pore solution. According to the point defect model (PDM) [24, 25], the higher donor density means that the passive films are more sensitive to pitting corrosion. Consequently, the results presented in Figure. 8 suggest the passivity of stainless steel is significantly degraded by the increasing deformation and concentration of Cl<sup>-</sup>.



**Figure 8.** Donor density of deformed 304 stainless steel in the carbonated concrete pore solutions (pH=9) at a frequency of 1000 Hz

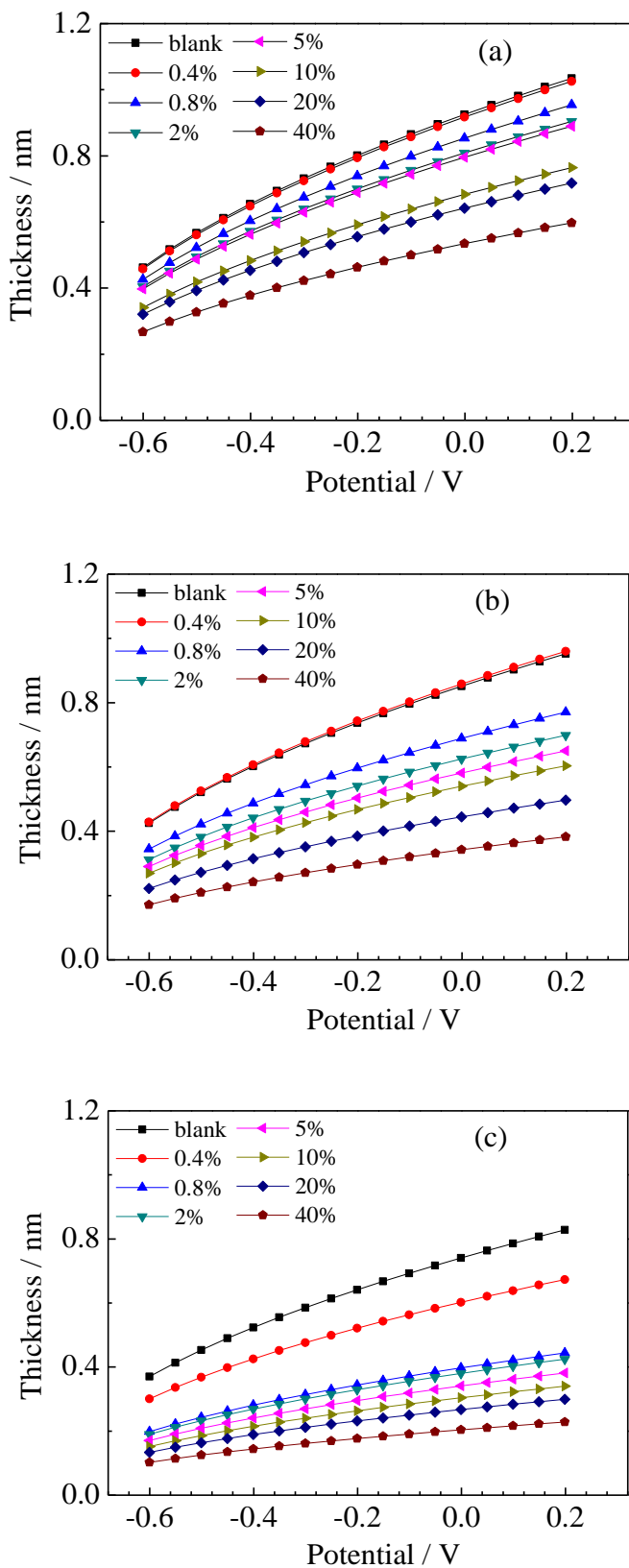
As earlier research [26, 27] has reported, the thickness of space-charge layer ( $W$ ) can be calculated from Eqs. (2)

$$W = \left[ \frac{2\epsilon\epsilon_0}{qN_D} \left( E - E_{FB} - \frac{KT}{q} \right) \right]^{\frac{1}{2}} \quad (2)$$

The results of  $W$  are presented in Figure. 9. As can be seen, the thickness of passive films on the stainless steel significantly decreased with the deformation degree. On the other hand, the passive film also became thinner as the concentration of Cl<sup>-</sup> increasing. The thinner space-charge layer accelerates the rate of the transport of the oxygen vacancies in the passive film [22], which would enhance the kinetic constant of the mediator oxidation on the 304 stainless steel [28]. Therefore, the

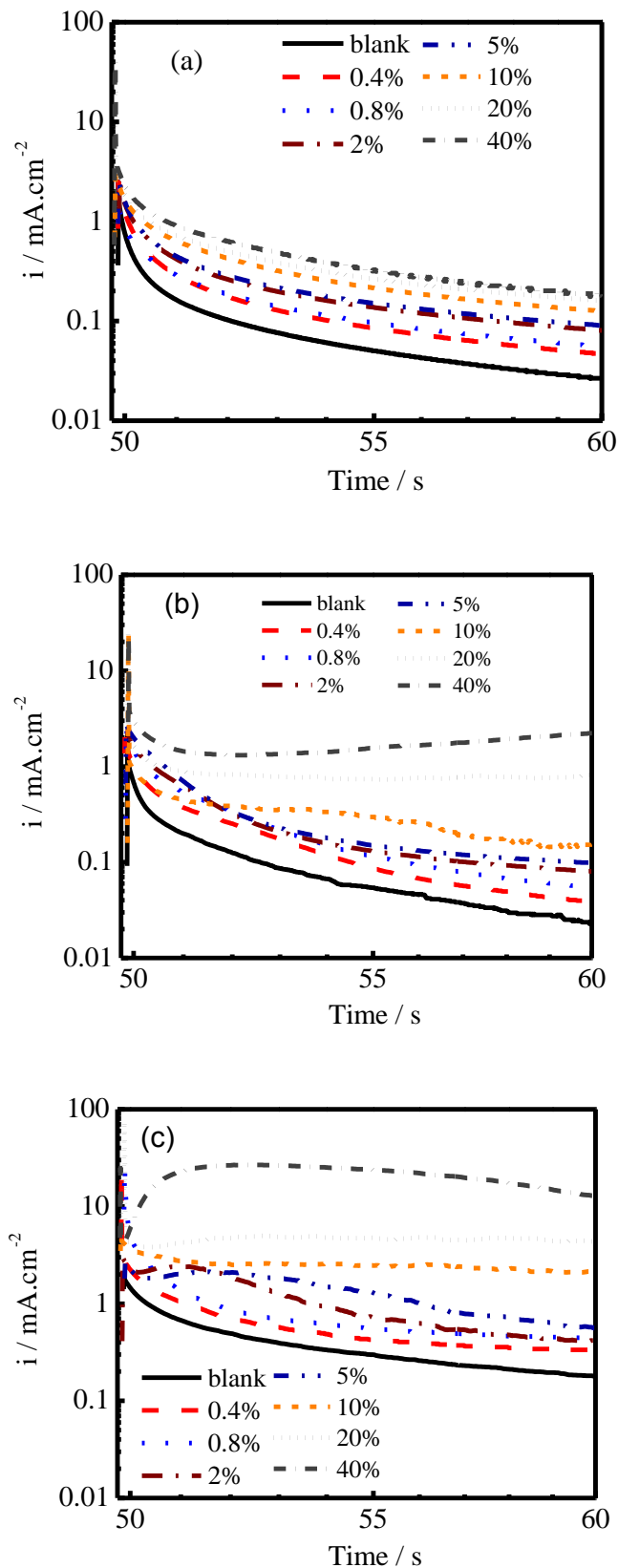


activity of AISI 304 stainless steel increased with the magnitude of deformation and concentration of  $\text{Cl}^-$ .



**Figure 9.** The thickness of the space charge layers of deformed 304 stainless steel in carbonated concrete pore solutions (pH=9), (a) without  $\text{Cl}^-$ , (b) 0.05 mol/L  $\text{Cl}^-$ , (c) 0.5 mol/L  $\text{Cl}^-$ .

3.4 Potential Step



**Figure 10.** Current-time variations of the deformed 304 stainless steel during potentiostatic polarization at 0.5 V in the carbonate concrete pore solution.

The current transient curves of deformed samples are presented in Figure. 10. As the results show, the current density of stainless steel obviously increased with the increasing deformation. Comparing with the control samples, the current density of the most seriously deformed samples (40%) almost one order of magnitude higher than that of the former. Moreover, as the concentration of  $\text{Cl}^-$  increasing, the current density of stainless steel also significantly increased. The current transient results, together with the OCP (Figure. 2), EIS (Figure. 5, Figure. 6), and the Mott-Schottky results (Figure. 8, Figure. 9), suggesting that the activity of AISI 304 stainless steel are significantly increased by the deformation and the aggressive ions ( $\text{Cl}^-$ ). The situation also means that the deformed stainless steel in the carbonated pore solution are more sensitive to pitting corrosion.

#### 4. CONCLUSIONS

The corrosion behavior of deformed AISI 304 stainless steel in a simulated carbonated concrete pore solution was studied. The following conclusions can be drawn:

(1) The values of OCP and impedance of stainless steel decreased with the increasing degree of deformation. The passive films of the stainless steel are heavy doped when the sample experienced serious deformation. The space-charge layer also became thinner as the magnitude of deformation increasing.

(2) With increasing concentration of aggressive ions ( $\text{Cl}^-$ ), the stability of passive film is obviously degraded, while the activity of stainless steel is significantly increased.

(3) A synergistic effect of deformation and aggressive ions ( $\text{Cl}^-$ ) on the degradation of passive film on stainless steel in the carbonated concrete pore solution is observed.

#### ACKNOWLEDGEMENTS

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