



# The effect of simulated concrete pore solution composition and chlorides on the electronic properties of passive films on carbon steel rebar



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## ABSTRACT

Effects of simulated concrete pore solution composition, pH, and added chlorides on electronic properties of passive films on carbon steel rebar were investigated using Mott–Schottky (M–S) analysis. Passive films showed n-type semiconductive behavior with two discrete donor species and high donor densities. Deep donor densities increased with increasing passivation time. Less protective films resulted in lower space charge capacitances and lower flatband potentials. Sulfates had little influence on electronic properties. Chlorides caused a loss of linearity of M–S plots. This loss of linearity required higher chloride levels and longer exposure times to occur in higher pH solutions.

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## 1. Introduction

Passivity and corrosion of carbon steel in the alkaline environment provided by concrete pore solutions (pH > 13) have been studied extensively using electrochemical techniques [1–12]. More recently, a number of studies has focused on the investigation of nano-scale properties and atomic structure of the passive films that form on carbon steel in highly alkaline environments. For example, Sánchez-Moreno et al. [13] proposed a two-layered passive film that is composed of an inner layer of mixed iron oxides with a stoichiometry similar to that of magnetite (i.e., Fe<sub>3</sub>O<sub>4</sub> or FeO + Fe<sub>2</sub>O<sub>3</sub>) and an external layer that is mainly composed of Fe<sup>III</sup> oxides. A similar structure was proposed by Joiret et al. [14] who used in-situ Raman spectroscopy to study passive film structure on carbon steel exposed to NaOH solutions. Sánchez et al. [15] also showed that the formation of the passive film occurred in two stages: The first stage, which takes place within hours of exposure of the iron substrate to simulated pores solution, was hypothesized to be related to the formation of an Fe<sup>II</sup> oxide layer. The second stage was proposed to be related to the thickening of the film. Furthermore, X-ray Photoelectron Spectroscopy (XPS) [16,17] and Electron Energy Loss

Spectroscopy (EELS) [18] investigations found that the thickness of the oxide films that form on carbon steel in the passivating environment of concrete pore solutions was typically in the range of 3–15 nm. As suggested by others, these studies also reported that near the film/substrate interface the film contained mostly Fe<sup>II</sup> oxides/oxyhydroxides while the layers near the free surface of the film mostly contained Fe<sup>III</sup> oxides/oxyhydroxides. Furthermore, the Fe<sup>II</sup>-rich zone near the steel–film interface was found to be thin (~2–3 nm) but protective; the Fe<sup>III</sup>-rich zone was thicker (~10–15 nm) but unprotective. This two-stage model is in agreement with theoretical passivity models that are based on an inner barrier layer that forms directly on metal substrate, and outer layer that precipitate through the hydrolysis of cations ejected from the inner layer [19,20].

Although considerable progress has been made towards a comprehensive understanding of electrochemical and nano-scale structural properties of passive films of carbon steel in concrete, electronic (semi-conductive) properties of these films have not been studied extensively despite the fact that past studies have found strong correlation between the electronic properties of passive films and their corrosion behavior [21,22]. For example, Schmuki and Bohni [23,24] and Hakiki et al. [25,26] correlated the electronic properties to the susceptibility of pitting corrosion of stainless steels. Szklarska-Smialowska [27,28] and Liu et al. [29] showed that similar correlations exist for the passive films of alu-

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minimum. Although a number of studies exist for stainless steels [30–33] in alkaline media, these studies were not typically representative of the passive films of carbon steel and of concrete pore solutions. Cheng and Luo [34,35], Hamadou et al. [36] and Li et al. [37] evaluated the electronic properties of carbon steel, but not in environments representative of those in concrete. Sánchez et al. [15,19] demonstrated that the passive film showed an n-type semiconductive behavior as part of a study on electrochemical properties of carbon steel rebar in a simulated concrete pore solution. More recently, the effect of strain and the use of inhibitors on the electronic properties of the steel rebar passive film in highly alkaline environments have been investigated [38,39].

The most common method for determining the electronic properties of semiconductive passive films is called Mott–Schottky (M–S) analysis [40]. This method, which is based on the Mott–Schottky equation [41–43], is implemented by measuring the capacitance of an electrochemical system as a function of applied potential. As shown in a recent study [44], however, the application of M–S analysis to carbon steel rebar in simulated concrete pore solutions involves a number of special considerations, which include the passive film formation method, passivation time, the M–S potential sweep rate, range, and direction, as well as the frequency of measurements. For example, when performing M–S analysis, most studies apply a formation potential to the sample to artificially form the passive film quickly (within hours) [47–49]. Although this approach works well for most applications, in reality, it is not valid for rebar in concrete since the passive film on carbon steel in concrete forms under open-circuit conditions and usually takes around two weeks to form fully [2,6,50]. As an outcome of aforementioned study [44], a methodology for using M–S analysis to study the electronic properties of passive films that form on carbon steel in highly alkaline solutions was developed; the current investigation also adopts this methodology, which is described later in the paper.

The main objective of this paper is to investigate the effects of electrolyte composition, pH and passivation time on the electronic properties of the passive films that form on carbon steel in simulated concrete pore solutions. It has been shown that pore solution composition, which can vary significantly depending on the types of cement and concrete, has a direct effect on the passive behavior and chloride-induced depassivation of carbon steel [1,2,7,10]. The effect of chlorides on the electronic properties of passive films are also investigated. The results of this investigation are also discussed within the scope of recent developments on the nanoscale properties and atomic structure of passive films that form on carbon steel in concrete pore solutions.

## 2. Materials and methods

### 2.1. Specimen preparation

As-received 2-mm-thick disc samples were cut out of US #5 (15.5 mm diameter) carbon steel rebar with an elemental composition that is provided in Table 1. After cutting to size, the samples were cleaned with acetone to remove machining greases and oils and rinsed with deionized water. The samples were then immersed in an ultrasonic bath of 5% acetic acid solution, followed by a second rinsing with deionized water. Next, the samples were ground with progressively increasing grit sizes, followed by a polish to 0.05  $\mu\text{m}$  using silica polish. This gave the samples a mirror finish with no noticeable scratches or blemishes. The samples were then rinsed with distilled water, dried with a delicate task wipe, and then immediately placed into a dessicator with silica dessicant gels until use.

**Table 1**

Composition of tested steel specimens (average of three spectrographic results).

Element	Weight (%)
C	0.26
Si	0.27
Mn	1.10
Cr	0.05
Ni	0.07
Mo	<0.01
Cu	0.21
Al	<0.005
Nb	<0.01
V	<0.005
Ti	<0.005
B	<0.0005
P	0.01
Si	0.03
W	<0.01
Sn	0.021
Co	0.01
Zr	<0.01
Fe	Balance

### 2.2. Experimental setup

Two identical three-probe electrochemical cells were used for testing. A Gamry Reference 3000 potentiostat and a Gamry Multiplexor were used for taking all electrochemical measurements. Gamry Echem software was used for analyzing impedance data. A graphite counter electrode with a high surface area and an Accu-met saturated calomel reference electrode (SCE) were used in all electrochemical measurements. The tip of the reference electrode was placed approximately 5 mm from the surface of the sample. All potentials reported in this study are shown versus SCE.

Each sample was loaded into the Princeton Applied Research K0105 sample holder, which is designed for performing repeatable and reliable electrochemical measurements on one of the exposed cut and prepared surfaces. The sample holder had hydrophobic Teflon washers to protect the sample edges from crevice corrosion; no crevice corrosion was observed in the tested samples during experiments. The exposed surface area after the sample was loaded into the holder was 1.15  $\text{cm}^2$ . The total resistance of the sample holder assembly was less than 1  $\Omega$ . The sample holder was immersed in a 1 L electrochemical cell with separate ports for reference and counter electrodes.

Three electrolytes were used for comparison in this study. The first is a saturated  $\text{Ca}(\text{OH})_2$  solution (pH 12.5), the second was a more representative concrete pore solution with  $\text{Ca}^+$ ,  $\text{K}^+$ , and  $\text{Na}^+$  ion additions (pH 13.4), and the final solution was identical to the second, except with the addition of  $\text{CaSO}_4$  (pH 13.3) to observe the effect of sulfates on the electronic properties of the passive film. In reality, concrete pore solution is a complex electrolyte that is composed of saturated levels of  $\text{Ca}(\text{OH})_2$  and many other ions and species [45–47]. The electrolytes that are used in the present work do not necessarily contain all possible species that exist in concrete pore solutions, but rather simulate them so that the effect of pore solution composition on the electronic properties of passive films that form on carbon steel can be studied in a systematic and controlled way. Major ionic species in the simulated concrete pore solutions that are used in this study include  $\text{Ca}^{2+}$ ,  $\text{Na}^+$  and  $\text{K}^+$ ,  $\text{OH}^-$ , and  $\text{SO}_4^{2-}$ , whereby sodium and potassium ions originate from alkali oxides such as  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$  that exist in ordinary portland cements. It has been documented that small amounts of sulfate ions (typically in the range of 1–4%wt.) exist in typical concrete pore solutions after the disappearance of the initial ettringite and monosulfate phases during the early stages of cement hydration [46,48,49]. Sulfate ions can originate from gypsum added during cement production, contaminated aggregates, or mixing water [48].

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