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## Oxygen Reduction on Passive Steel and Cr Rich Alloys for Concrete Reinforcement

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**Abstract:** Mature passive films (age > 10<sup>6</sup> s) were grown in aerated saturated calcium hydroxide solution, at the open circuit, on plain steel and alloys with 9% and 22% Cr, as well as austenitic stainless steels. The materials were commercially produced concrete reinforcing steels. Differences in the polarization of the oxygen reduction reaction were evidenced. Oxygen reduction rates at moderate cathodic polarization were found to approximate ideal Tafel behavior, to be greatest for plain steel and to decrease with increasing Cr content. Mott-Schottky analysis indicated n-type semiconductor behavior in all cases, with higher apparent donor density for the plain steel and little differentiation between the other materials.

**Keywords:** Oxygen reduction, chromium, passive, capacitance, semiconductor

### 1. Introduction

Steel reinforcement in concrete normally remains passive due to contact with highly alkaline pore water (pH>~12.5). Chloride ion contamination above a threshold value can induce localized reinforcement corrosion, where much of the cathodic reaction is oxygen reduction on surrounding passive steel surfaces [1]. Stainless and other Cr-containing steels have a higher corrosion initiation threshold and are being increasingly used instead of plain steel in concrete subject to aggressive service conditions [2]. An added benefit of using Cr steels is that, for a given cathodic polarization potential, the rate of the oxygen

reduction reaction can be significantly lower than for plain steel [3] with consequent lessening of severity of localized corrosion should it eventually start. However, little information is available on the mechanism responsible for this decrease and on its dependence on alloying content. It has been speculated [3] that the decreased cathodic reaction rate reflects lowered conductivity of the passive film but the supporting experimental evidence is limited. To address these issues the electrochemical behavior of the passive films in alkaline solution was examined here for series of commercial reinforcing steel alloys spanning a wide composition range.

## 2. Experimental

### *Materials, test solution and electrochemical procedures*

Commercial corrugated reinforcing steel stock was used, turned to 9mm diameter. The alloys were ASTM A-615 plain steel (PS), a proprietary alloy with ~9 wt% Cr (9 Cr), a duplex, low Mo ferritic-austenitic stainless steel (2201), and two 316L stainless steel (316-1 and 316-2) (Table 1). Cross section slices of each alloy were embedded together but mutually isolated in a 40 mm diameter metallographic epoxide holder and ground to an F-4000 grit finish. Immediately after surface grinding the assembly was ultrasonically cleaned in methanol, dried, and immersed in saturated  $\text{Ca}(\text{OH})_2$  solution (pH~12.6) aerated with decarbonated air. The sensing point of the reference electrode was placed about 6 mm away from the center of the specimen cluster. The sensing tip was either a Luggin probe extended from an Ag/AgCl (1M KCl) reference electrode (RE) -in which scale all potentials are reported in this paper- or alternatively a 1-cm long gold wire periodically calibrated against the RE. The counter electrode was a 25mmx25mm platinum sheet. Temperature was  $\sim 22^\circ \pm 3^\circ \text{C}$ .

The steel surfaces were allowed to evolve at the open circuit potential (OCP) except for electrochemical evaluations conducted after ~1 wk and ~4 wk immersion. Evaluation included OCP electrochemical impedance spectroscopy (EIS), cyclic cathodic (starting at OCP) potentiodynamic polarization at a scan rate of 0.167 mV/sec, and apparent capacitance measurements (simply evaluated from the imaginary component of the impedance) at 10 Hz and 1 kHz also during cathodic excursions from OCP. Cathodic excursions extended no further than -0.5 V, to represent the potential range normally experienced in atmospherically exposed reinforced concrete. Following the tests at ~4wk immersion, the test cell was temporarily deaerated with flowing  $\text{N}_2$  and the tests repeated in the deaerated condition. All tests were at least in duplicate and results shown are typical of replicate behavior.

Table 1 Chemical composition of alloys used (wt%)

Alloy	Cr	Ni	Mo	C	S	P	Mn	Si	Cu
PS	0.14	0.09	0.017	0.41	0.054	0.017	0.85	0.18	0.4
9 Cr	9.3	0.1	0.03	0.05	0.015	0.012	0.45	0.23	0.12
2201	21.57	1.74	0.24	0.03	0.001	0.019	4.73	0.78	0.34
316-1	17.57	10.22	2.08	0.03	0.002	0.027	1.57	0.57	0.36
316-2	16.17	10.24	2.15	0.03	0.007	0.029	1.62	0.4	0.75

### 3. Results and Discussion

All alloys showed significant ennoblement during the first few days of exposure, indicating slow maturing of the passive film. The PS potential evolved toward terminal values in the order of  $-0.1\text{V}$ , typical of those normally observed in concrete and aerated simulated pore solution [1]. The stainless steels evolved toward terminal potentials about  $0.1\text{V}$  or  $0.2\text{V}$  lower, also as commonly observed. The 9 Cr potentials were comparable to those of the stainless steels. Terminal potentials of replicate specimens were in the same order but showed some variability ascribed to incipient crevice corrosion at the perimeter in contact with the embedding epoxide.

The potentiodynamic tests showed essentially the same behavior (Figure 1) after  $\sim 1\text{wk}$  or  $\sim 4\text{wk}$  exposure to the aerated solution. For cathodic polarization beyond  $\sim 0.1\text{V}$  from the OCP all alloys displayed approximately linear (less so for PS)  $E\text{-log } i$  behavior with apparent Tafel slope  $\sim 0.12\text{V}$  for PS and 9 Cr and  $\sim 0.16\text{V}$  for the stainless steels. There was relatively little hysteresis in all cases in that polarization regime. The greater deviation from Tafel behavior for PS, which had by far the greatest cathodic current densities ( $\sim 20\text{-}30\ \mu\text{A}/\text{cm}^2$  at  $-0.5\text{V}$ , Figure 2) may be an indication of the onset of concentration polarization. The 9 Cr had intermediate cathodic current densities while the stainless steels had as a group very low and comparable cathodic current density. While Cr content, appears to be the main factor (Figure 2), a somewhat more uniform decreasing trend in cathodic current density is obtained when plotting against Cr+Ni, or total alloying content. Upon deaeration, all current densities decreased by 1-2 orders of magnitude. All currents returned to the former levels upon reaeration, indicating that the cathodic behavior under aeration reflected primarily oxygen reduction and not reduction of species in the passive film. This observation is in keeping with expected behavior based on previous work [4] that showed at  $\text{pH}\sim 13$  little reduction of passive films on iron at potentials  $> \sim -0.7\text{V}$ .

EIS measurements at the OCP showed a well-defined real high frequency impedance limit which was consistent with the expected value of the solution resistance  $R_s$  ( $\sim 60 \Omega$  with the cell configuration used). Results were comparable in the 1wk and 4wk tests. At  $< 100$  Hz the impedance could be closely described (after subtracting a nominal constant close to  $R_s$ ) by a parallel combination of a large polarization resistance and a constant phase angle element (CPE,  $Z=Y_0^{-1} (j\omega)^{-n}$  where  $\omega$  is the angular frequency) that was nearly ideally capacitive ( $n= 0.95-0.96$ ). The spectrum above 100 Hz could be approximated using the same equivalent circuit, but with  $n\sim 0.7$ . The greater frequency dispersion at higher frequencies likely reflects microscopic and macroscopic current distribution artifacts. Thus the Mott-Schottky analyses were reported only using the apparent capacitance  $C=1/(\omega \text{Im}(Z))$  calculated for 10 Hz where capacitive behavior was nearly ideal. It is noted that no systematic difference between the  $R_s$  values for PS and for the high Cr alloys was observed. The EIS behavior observed here is at variance with that described for similar systems by Abreu et al [3]. Those authors reported a high frequency loop with a resistive component (interpreted as a film resistance, but that was of the same order as the expected  $R_s$ ) that was greater for stainless steel than for PS.

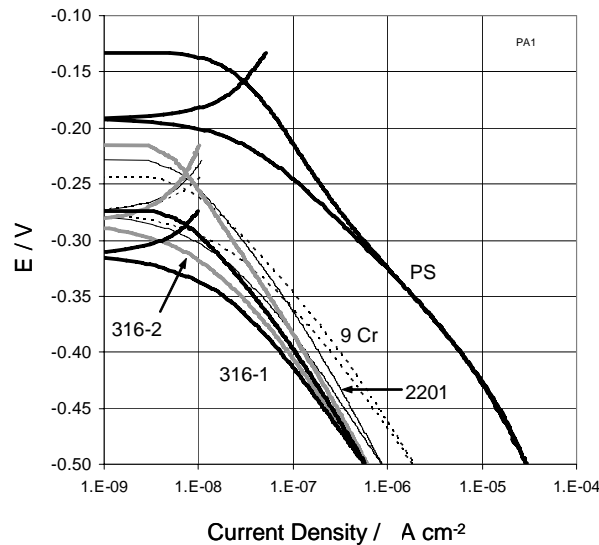


Fig. 1 Example of cyclic cathodic polarization curves. 1wk in aerated  $\text{Ca}(\text{OH})_2$ .

The Mott-Schottky plots (Figure 3) showed usually linear regions with slope indicative of n-type behavior and a common apparent flatband potential of  $\sim -0.7$  V for all alloys. Apparent donor densities  $N_d$  were calculated from the slopes assuming a dielectric constant = 10 with results shown in Figure 2. Artifacts may exist from neglecting Helmholtz interfacial capacitance since total

capacitance is relatively large (in the order of 20-30  $\mu\text{F}/\text{cm}^2$  at the OCP), and from the very narrow ( $\sim 0.5$  nm) depletion zone thickness calculated from the same data. Nevertheless, the resulting Nd values although large are consistent with those observed by other investigators [5]. It should be noted also that actual capacitances and donor densities may be somewhat lower than the nominal values obtained, since the calculations ignored the exaggerating effect of surface roughness.

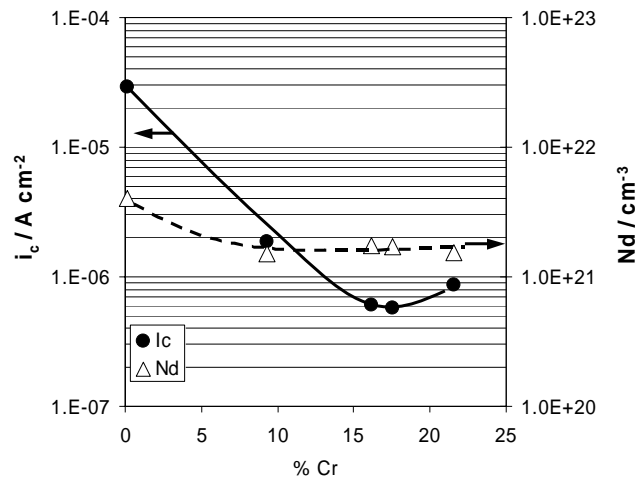


Figure 2. Cathodic current density  $i_c$  at  $-0.5$  V, and apparent donor density Nd from 10 Hz Mott-Schottky analysis as function of Cr content. 1 wk in aerated  $\text{Ca}(\text{OH})_2$ .

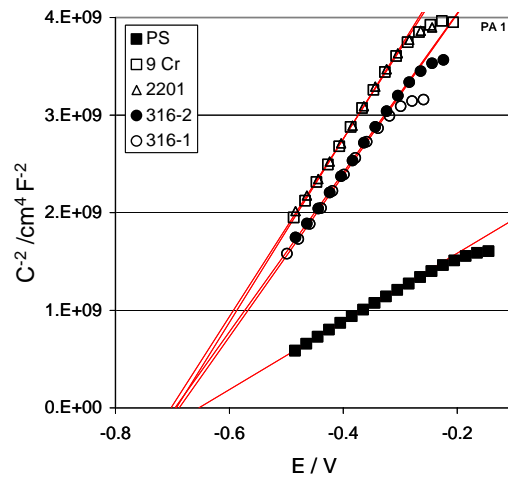


Figure 3. Mott-Schottky analysis. The solid lines indicate slope and extrapolation based on data starting  $\sim 50$  mV below OCP. 1 wk in aerated  $\text{Ca}(\text{OH})_2$ .

In contrast with the large variations in cathodic polarizability, Nd was greater by only about a factor of 2 for PS than for the Cr alloys. There is almost no differentiation in Nd between the Cr alloys themselves, and no dramatic difference in the apparent flatband potential value of any of the alloys. The higher current densities in PS may reflect the thinner depletion layer (and associated nonlinear increase in electronic current) consistent with the noted differences in donor density. It may also be speculated that in the Cr alloys an outer n-type layer rich in Fe oxides is present, coupled with an inner Cr-oxide rich layer that would be expected to have p-character [6]. Such configuration may possibly require additional polarization (with respect to a plain steel case) to achieve a given current level. Investigation of these issues continues.

#### 4. Summary

Oxygen reduction rates at moderate cathodic polarization were found to approximate ideal Tafel behavior, to be greatest for plain steel and to decrease with increasing Cr content. The results indicate that the cathodic current under naturally aerated conditions stemmed from oxygen reduction with little if any contribution from the reduction of oxide formed at potentials typical of steel in atmospherically exposed concrete. Mott-Schottky analysis indicated n-type semiconductor behavior in all cases, with higher apparent donor density for the plain steel and little differentiation between the other materials.

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