



INVESTIGATION OF ASCORBIC ACID INFLUENCE ON STEEL PASSIVITY IN SAT. $\text{Ca}(\text{OH})_2$



Lidija Valek^{**}, Sanja Martinez^{*}, Marijana Serdar^b

^{*}Department of Electrochemistry, Faculty of Chemical Engineering and Technology, Marulićev trg 19, 10000 Zagreb, Croatia, lvalek@fkit.hr, sanja.martinez@fkit.hr;
^bFaculty of Civil Engineering, Kačićeva 26, 10000 Zagreb, Croatia, mserdar@grad.hr

INTRODUCTION

Characteristics of the passive film formed on steel in alkaline solutions are of major importance when considering the susceptibility to pitting corrosion. Presence of chelating agent may improve the performance of such film by competitive adsorption through formation of surface chelates that force chloride ions to interact with energetically less favorable sites, therefore requiring greater activation energy for pitting to occur.

The effect of the complexing agent, ascorbate anion, on the electrochemical behavior and semiconductive properties of passive film formed on non alloyed steel in deaerated saturated $\text{Ca}(\text{OH})_2$ was investigated in this study.

RESULTS

Cyclic voltammetry results

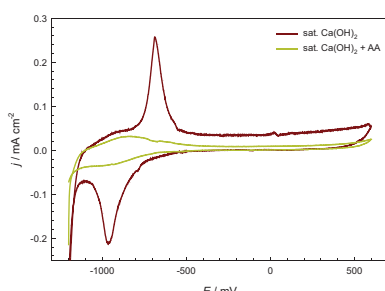


Figure 1. Cyclic voltammogram of steel in sat. $\text{Ca}(\text{OH})_2$ with and without addition of 10^{-3} M AA, scan rate of 10 mV s^{-1} (2^{nd} cycle).

EIS results

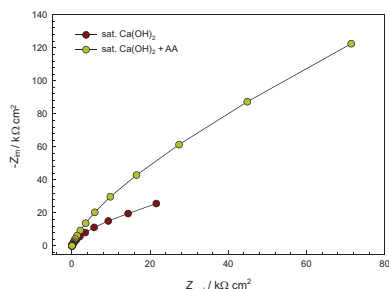


Figure 2. Nyquist plots of the impedance spectra of steel in sat. $\text{Ca}(\text{OH})_2$ with and without addition of 10^{-3} M AA.

Table 1. Parameters determined by fitting the EIS data shown in Fig. 2. to the simple equivalent electrical circuit.

	sat. $\text{Ca}(\text{OH})_2$	sat. $\text{Ca}(\text{OH})_2 + 10^{-3}$ M AA
$R_a / \Omega \text{ cm}^2$	23	24
$C_{dl} / \mu\text{F cm}^{-2}$	3.248×10^{-4}	2.573×10^{-4}
n	0.886	0.886
$R_{ct} / \text{k}\Omega \text{ cm}^2$	43.3	253.7

CONCLUSIONS

Cyclic voltammetry measurements showed that presence of AA in the solution suppressed the oxidation and reduction peaks, lowering the current in the passive region. Electrochemical impedance spectroscopy revealed that the processes at the interface at the open circuit potential are charge transfer controlled with significantly higher charge transfer resistance in AA presence. ATR FTIR measurements confirmed presence of ascorbate chelate at the steel surface after exposure to the sat. $\text{Ca}(\text{OH})_2$ with addition of AA.

It has been reported in the literature that passive film formed on steel consists of inner barrier layer (Fe_2O_3) and precipitated outer layer ($\gamma\text{-Fe}_2\text{O}_3$). Film formed at anodic potentials in the passive region (-100 to 300 mV) was removed layer by layer by galvanostatic cathodic reduction. Potential arrest at approximately $-900 \text{ mV}_{\text{SCE}}$ commonly attributed to the reduction of $\gamma\text{-Fe}_2\text{O}_3$ to $\text{Fe}(\text{II})$ appeared only in sat. $\text{Ca}(\text{OH})_2$. Reduction of film formed in the presence of AA appeared at more negative cathodic potentials with less charge due to the lower concentration of ferrous ion in the surface layer. Growth of anodic films by galvanostatic oxidation starting from the same pre-existing films as in the case of reduction was studied. In the presence of AA, longer formation times were observed before the oxygen evolution potential was reached. Presence of chelating agent adsorbed at the oxide surface probably hinders formation of the precipitated outer layer and thus results in shorter reduction times and longer oxidation times. Mott Schottky experiments were performed in order to investigate semiconducting properties of passive film. The electronic character of passive film formed in sat. $\text{Ca}(\text{OH})_2$ with and without AA was found to be n-type which is consistent with the dominant defects being oxygen vacancies and cation interstitials. Using dielectric constant assumption, semiquantitative defect densities were calculated. The defect concentration was found to decrease with increasing the film formation potential. Mott Schottky analysis showed lower defect density of the passive film formed in the presence of AA.

Mott Schottky analysis

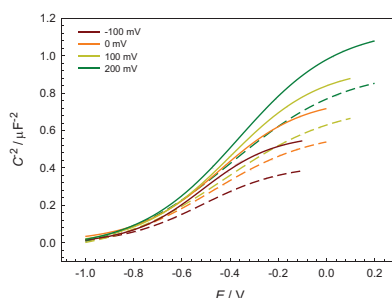


Figure 3. Mott Schottky plots for the passive film on steel at different potentials for 20 minutes in sat. $\text{Ca}(\text{OH})_2$ with (—) and without (---) addition of 10^{-3} M AA.

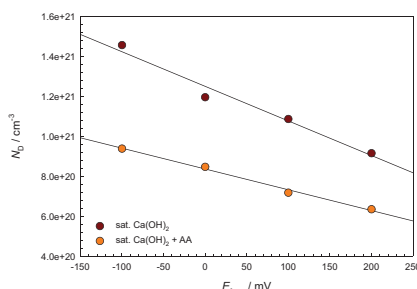


Figure 4. Donor concentration, N_d , of the oxide film formed on steel at different potentials in sat. $\text{Ca}(\text{OH})_2$ with and without addition of 10^{-3} M AA.

FTIR results

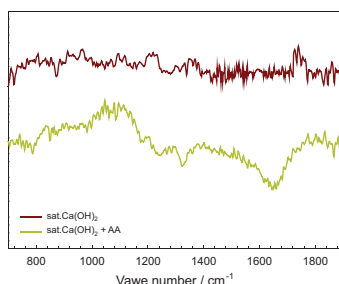


Figure 7. ATR FTIR spectra of the steel surface after formation of the passive film in deaerated sat. $\text{Ca}(\text{OH})_2$ with and without addition of 10^{-3} M AA.

Galvanostatic reduction and oxidation of oxide film

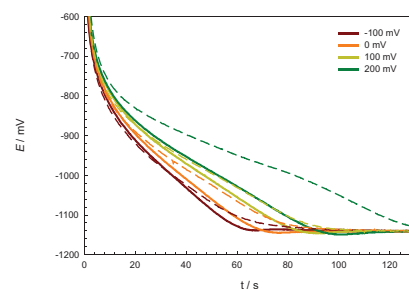


Figure 5. Galvanostatic reduction curves ($j = -25 \mu\text{A cm}^{-2}$) for the oxide film formed on steel at different formation potentials for 20 minutes in sat. $\text{Ca}(\text{OH})_2$ with (—) and without (---) addition of 10^{-3} M AA.

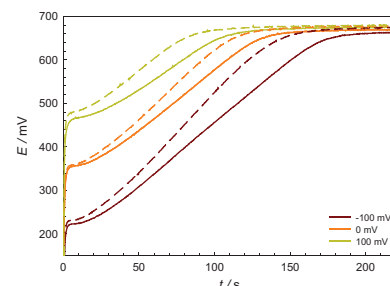


Figure 6. Galvanostatic oxidation curves ($j = 25 \mu\text{A cm}^{-2}$) for the oxide film formed on steel at different formation potentials for 20 minutes in sat. $\text{Ca}(\text{OH})_2$ with (—) and without (---) addition of 10^{-3} M AA.

EXPERIMENTAL

ELECTRODES:

- WE: non alloy special prestressing steel (EN 10020)
- pretreatment: abraded by grit 600 and 1200 emery paper, rinsed in ethanol
- CE: graphite rod
- RE: SCE

ELETOLYTE: deaerated saturated $\text{Ca}(\text{OH})_2 + 10^{-3}$ M ascorbic acid (AA)

ELECTROCHEMICAL SETUP: PAR VMP2 potentiostat/galvanostat with VMP3/Z impedance option

TECHNIQUES:

- CYCLIC VOLTAMMETRY - $v = 10 \text{ mV s}^{-1}$, 3 cycles
- ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY - $f = 100 \text{ kHz} - 10 \text{ mHz}$, ampl. 10 mV
- MOTT SCHOTTKY ANALYSIS - $f = 1 \text{ kHz}$, form. pot.: $-0.1 \text{ V} - 0.2 \text{ V}$
- GALVANOSTATIC REDUCTION AND OXIDATION - $j = 25 \mu\text{A cm}^{-2}$, Form. pot.: $-0.1 \text{ V} - 0.3 \text{ V}$