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Short Communication

On Metastable and Stable Pitting Corrosion of Zinc in Perchlorate- and Chlorate-Containing Sodium Hydroxide Solutions

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Metastable and stable pitting corrosion behaviour of Zn in 0.5 M NaOH solutions containing various concentrations (0.01 – 0.1 M) of ClO_3^- or ClO_4^- anions was studied. Measurements were conducted by means of potentiodynamic anodic polarization technique, complemented with *ex situ* SEM and AFM examinations. Addition of either ClO_3^- or ClO_4^- stimulated general corrosion and ruptured the passive layer to an extent depending on the type and concentration of the tested anion. Experimental findings confirmed that metastable pitting events (appeared as oscillations in current at potentials close to the pitting potential, E_{pit}) was mainly due to Cl^- ions (produced via the reduction of ClO_3^- and ClO_4^-). Thus, Cl^- is the aggressive ion that caused metastable pitting and not ClO_3^- and ClO_4^-. However, ClO_3^- and ClO_4^- anions were found to induce stable pitting even in absence of Cl^- ions, with ClO_3^- being more aggressive than ClO_4^-. A cooperative influence between Cl^- and either ClO_3^- or ClO_4^- in passivity breakdown and pitting initiation is confirmed and discussed.

Keywords: Zinc; Pitting; Chlorate; Perchlorate; SEM; AFM

1. INTRODUCTION

Metastable pitting of metals and alloys, appeared as current oscillations near the pitting potential, have been studied by many authors [1–11]. The occurrence of these oscillations in current is explained by considering the occurrence of pitting corrosion, which finally results in the creation of local active areas (pits) on the passive electrode surface. The objective here, and in a continuation of our previous studies regarding passivity and passivity breakdown of Zn in some aqueous solutions [12-

15], is to apply potentiodynamic anodic polarization measurements to study passivity breakdown and pitting susceptibility of the Zn/OH^-/ClO_3^- and Zn/OH^-/ClO_4^- interfaces. An attempt is made to extend the use of current oscillations, that form at potentials well-below, but not far from, the pitting potential, to explain why ClO_3^- and ClO_4^- induce pitting corrosion to Zn, although both are large anions and therefore are not expected to occupy anion vacancies to initiate pitting corrosion according to the point defect model (PDM). Pitting corrosion due to Cl^- ions (produced via the reduction of ClO_3^- and ClO_4^-) is also considered based on PDM. Morphologies of pitted Zn surfaces were studied by SEM and AFM examinations.

2. EXPERIMENTAL

The working electrode employed in the present work was made of very pure zinc rod (99.99% Koch Light Laboratories, Colnbrook Buckes, UK) with an apparent surface area of 0.50 cm^2. Before each run, the electrode was successively ground to 2000 grit SiC paper. Electrochemical measurements were performed using Autolab frequency response analyzer (FRA) coupled to an Autolab Potentiostat/Galvanostat (PGSTAT30) with FRA2 module connected to a personal computer.

A volume of 100 ml was maintained in a three electrode electrochemical transparent polystyrene cell. A long Pt wire and a saturated calomel electrode (SCE) were used as counter (CE) and reference (RE) electrodes, respectively. Ohmic drops between the working electrode (WE) and the reference electrode are small in this cell and were compensated electronically by a feedback loop of a homemade potentiostat [6]. However, it is clear that a full compensation is not possible due to the localized attack and the high local current densities within the corrosion pits.

The experiments were carried out in 0.5 M NaOH solutions without and with various concentrations (0.01 – 0.1 M) of $NaClO_3$ or $NaClO_4$. These solutions were freshly prepared from analytical grade chemical reagents using water purified by a Millipore Milli-Qsystem, and were deaerated with N_2 for 20-25 min before each run. Measurements were carried out at $25 \pm 0.2\ ^oC$, while N_2 was passed over the solution.

Polarization curves were recorded by changing the electrode potential automatically from the starting potential (-2.0 V) up to anodic potentials at a scan rate of 10^{-4} V s^{-1} until stable pitting occurred. Prior to each run, the open circuit potential of the working electrode was measured as a function of time during 60 min. This time is found to be quite sufficient for the working electrode to reach a quasi-stationary value for the open circuit potential. Then, the electrode was potentiostatically hold at the starting potential for another 60 min period to achieve considerable amounts of Cl^- ions that liberated in solution as a result of the cathodic reduction of ClO_4^- and ClO_3^- anions. The concentrations of the libetrated Cl^- ions was determined potentiometrically using an Ag/AgCl selective electrode (with a detection limit of 10^{-6} M Cl^-) and a standard solution of $AgNO_3$ and a HANNA pH-meter model pH 211.

At least three separate experiments were carried out for each run to ensure reproducibility of results. The reproducibility of the polarization curves was good. This good reproducibility was expected since a protracted immersion period was undertaken to achieve a steady corrosion potential.

For microstructural studies by SEM (Analytical Scanning Electron Microscope JEOL JSM 6390 LA) and topographical characterizations by AFM (Veeco Multimode 8), some Zn samples were exposed to pitting attack in 0.5 M NaOH solution containing 0.05 M ClO_4^- or ClO_3^-. Each sample was held at the given potential for 5 min, and finally washed thoroughly.

3. RESULTS AND DISCUSSION

3.1. Influence of ClO_4^- and ClO_3^- anions on the anodic behaviour of Zn in NaOH

Potentiodynamic anodic polarization curves were recorded for Zn in 0.5 M NaOH solutions without and with various concenrations (0.01-0.1 M) of ClO_4^- or ClO_3^- anions as a function of the starting cathodic potential ($E_{s,c}$) at 25 ^oC. Some of the results obtained in presence of 0.05 M ClO_4^- or ClO_3^- are depicted in Figs. 1a and b as representative examples. Similar findings were obtained for the other tested concentrations (data not included here).

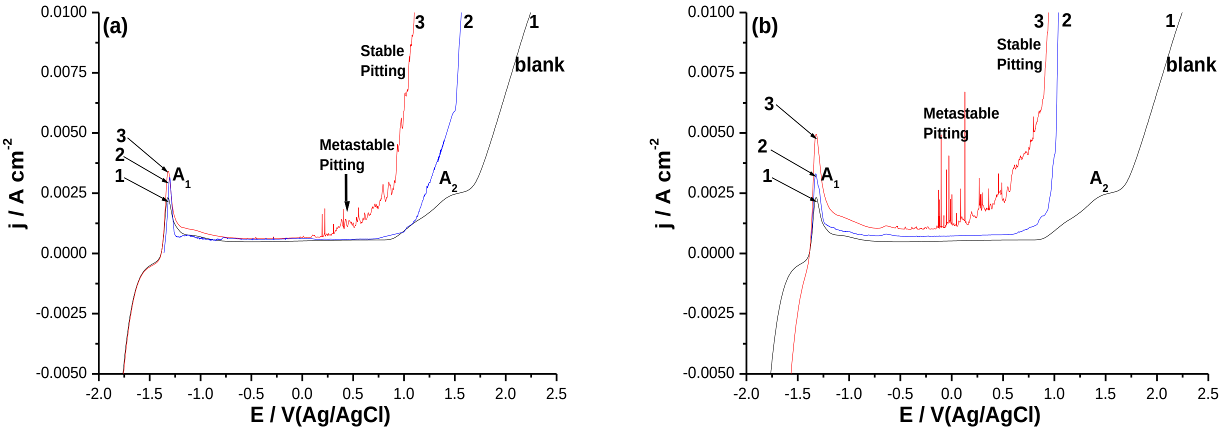


Figure1. Potentiodynamic anodic polarization curves recorded for Zn in 0.5 M NaOH solution without and with 0.05 M; a) ClO_4^- or b) ClO_3^- at a scan rate of 10^{-4} V s^{-1} at 25 ^oC. Curves 1 and 3 were swept starting from a cathodic potential of $E_{s,c}$ = -2 V. Curve 2 in each case was started from the respective corrosion potential.

It is obvious from Fig. 1 that in the absence of ClO_3^- and ClO_4^- anions (curve 1), the anodic span displays a well-defined anodic peak A_1, related to the formation of $Zn(OH)_2$ [16,17]. Peak A_1 is followed by a wide passive region which extends up to the appearance of the second anodic (shoulder) peak A_2 prior to oxygen evolution. Peak A_2 is assigned to the formation of the passive ZnO_2 film [16,17]. Addition of either ClO_3^- or ClO_4^- to the alkaline solution (curve 3) stimulates the anodic dissolution through peak A_1, and breaks down the passive layer and initiates pitting to an extend depending on $E_{s,c}$ and the type and concentration of the tested anion. Curve 2 in Figs. 1a and b is a special case and will be discussed later. This curve was swept starting from the corrosion potential (E_{corr}) to avoid the cathodic reduction of ClO_4^- and ClO_3^- anions to chlorides. Thus, the objective of this experiment, as will be seen, is to clarify the aggressive influence of such anions in absence of chlorides.

Referring again to curve 3, it is obvious that metastable pitting events result (see current fluctuations in the passive region), followed by stable pitting attack. The appearance of current fluctuations in the passive region is evidence that passivity is not stable, and indicative of pitting corrosion. The occurrence of these oscillations was explained by the consecutive formation and repassivation of microsize pits, indicating the formation of so-called metastable pits [4]. Metastable pitting events are pronounced and well-defined in case of ClO_3^- anion. ClO_3^- anion is therefore shown to be more aggressive than ClO_4^- anion towards passivity breakdown and initiation of pitting. The pitting potential (E_{pit}) is always more negative, and the passive current density (j_{pass}) is always higher, in presence of ClO_3^- than in presence of ClO_4^-.

3.2. Cathodic reduction of ClO_4^- and ClO_3^- anions and the role of the produced Cl^- ions

It has been shown that the reduction of ClO_4^- to chlorides (Eq. 1) plays a substantial role in metal corrosion studies [6-8,18,19].

$$ClO_4^- + 4H_2O + 8e^- = Cl^- + 8OH^- \qquad (1)$$

On the other hand, ClO_3^- is kinetically less stable in comparison to ClO_4^- [13]. These results are caused by the faster reduction of ClO_3^-, Eq. (2), to form aggressive Cl^- ions, compared with that of ClO_4^-.

$$ClO_4^- + 3H_2O + 6e^- = Cl^- + 6OH^- \qquad (2)$$

This faster reduction of ClO_3^- compared with that of ClO_4^- is confirmed here from the potentiometric determination of Cl^- using an Ag/AgCl selective electrode which showed that the concentration of the liberated Cl^- ions is always greater in presence of ClO_3^- than in presence of ClO_4^-. Therefore the reduction of ClO_3^- to Cl^- followed by pitting should occur much more readily in chlorate solutions. This may add another explanation why ClO_3^- is more aggressive than ClO_4^- towards passivity breakdown of Zn in these solutions.

A point defect model is employed to show the effect of electronic structure on pitting [20]. Based on this model, the liberated Cl^- ions incorporate to the passive film by occupying anion vacancies. This results in a decrease of anion vacancies and increases the cation vacancies. When the cation vacancies start to pile up at the metal interface, a breakdown of the passive film occurs.

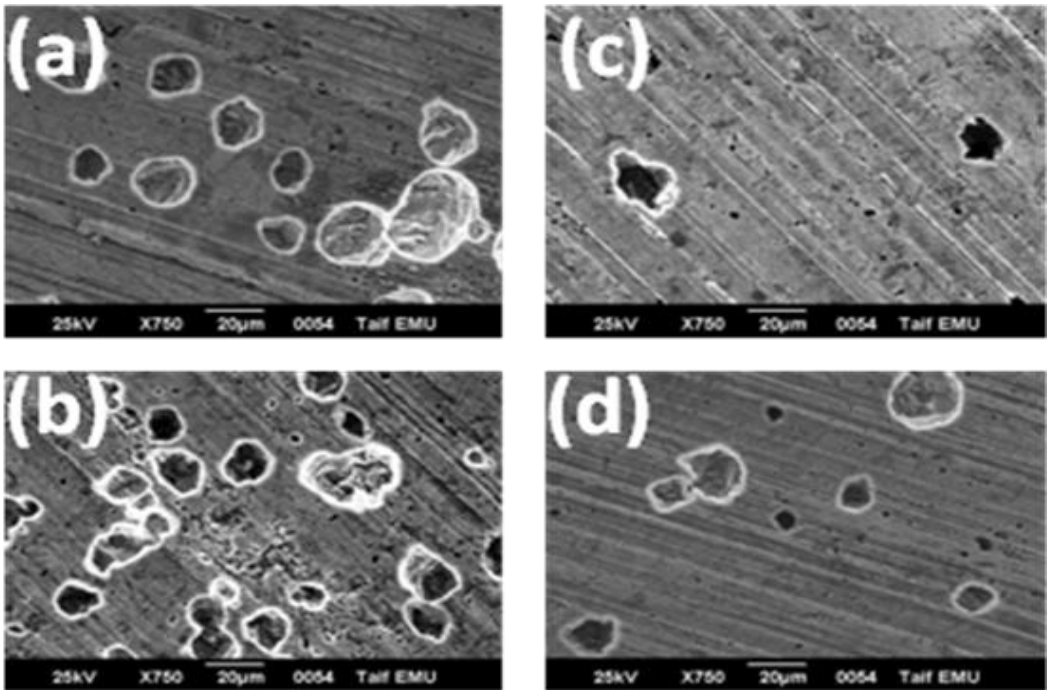
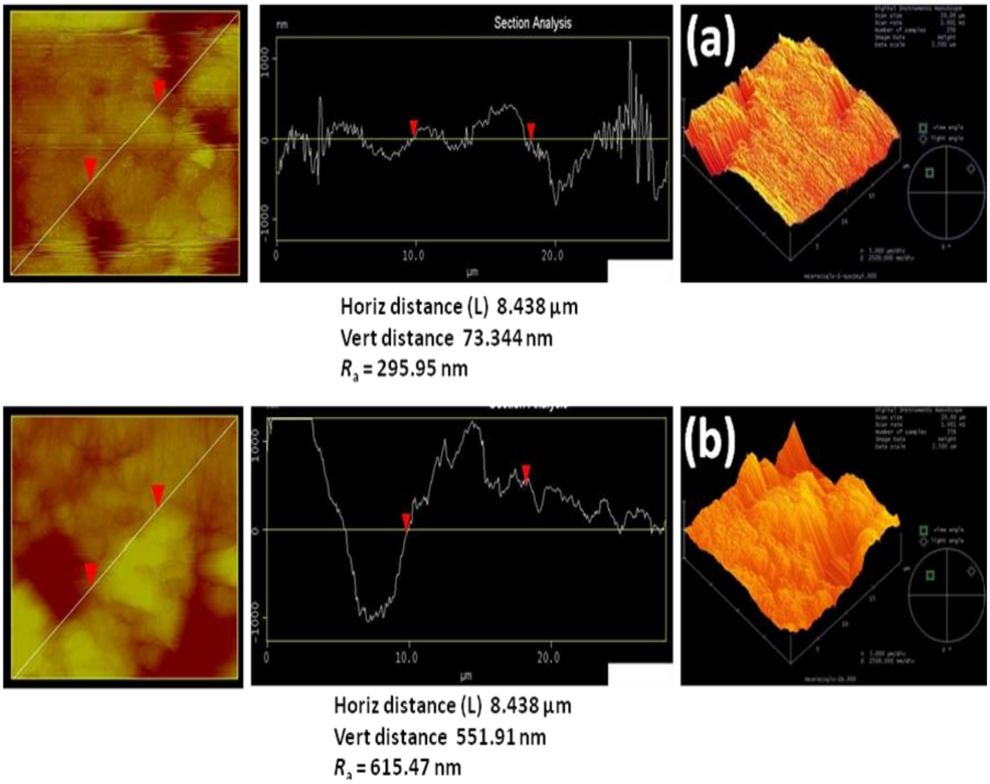
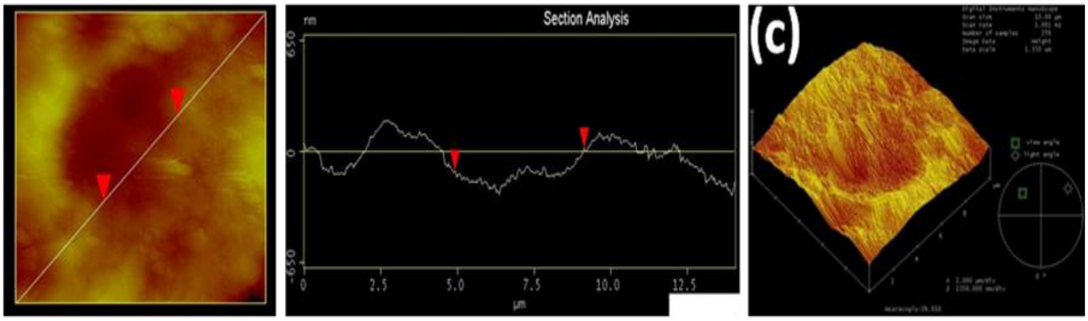
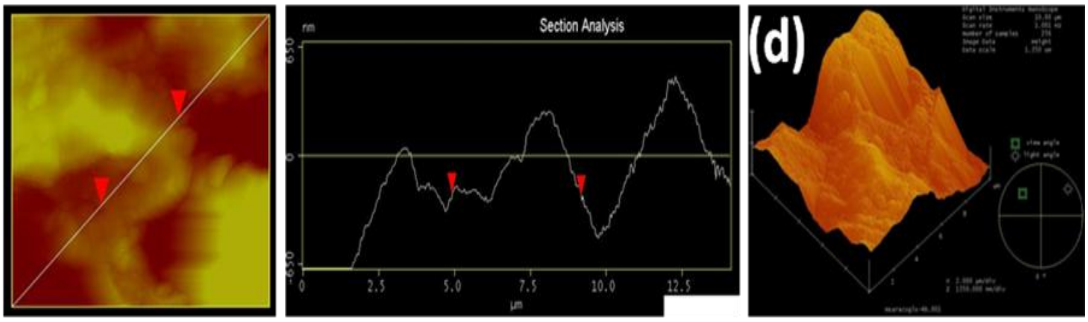


Figure 2. SEM micrographs recorded for Zn in 0.5 M NaOH solution containing 0.05 M (a,c) ClO_4^- or (b,d) ClO_3^-. The electrode is potentiodynamically polarized at a scan rate of 10^{-4} V s^{-1} starting form (a,b) $E_{s,c}$ = -2.0 V or (c,d) E_{corr} up to 1.0 V (i.e., beyond E_{pit} for all cases), then the electrode is potentiostatically held at 1.0 V for 5 min.





Horiz distance (L) 4.219 µm
Vert distance 130.62 nm
R_a = 115.16 nm



Horiz distance (L) 4.258 µm
Vert distance 56.844 nm
R_a = 381.29 nm

Figure 3. AFM images recorded for Zn in 0.5 M NaOH solution containing 0.05 M (a,c) ClO_4^- or (b,d) ClO_3^-. The electrode is potentiodynamically polarized at a scan rate of 10^{-4} V s^{-1} starting form (a,b) $E_{s,c}$ = -2.0 V or (c,d) E_{corr} up to 1.0 V (i.e., beyond E_{pit} for all cases), then the electrode is potentiostatically held at 1.0 V for 5 min. Each group of images includes: 2D-topographic image of the corroded coupon surface (left); sectional analysis determing surface roughness due to pitting

However, it is not wiser to exclude the role played by ClO_3^- and ClO_4^- anions, together with Cl^-, in passivity breakdown and initiation of pitting. The following points may clarify the aggressive influence of ClO_4^- and ClO_3^- anions and their contribution with Cl^- ions to rupture the passive layer:

(i) Zn is found to pit in ClO_4^-/NaOH and ClO_3^-/NaOH containing solutions, even when potentiodynamic anodic polarization was started from the corrosion potential (i.e., no cathodic reduction reaction and no Cl^- ions were detected); see curve 2 in Figs. 1a and b. It is seen that current oscillations disappeared when Cl^- is gone (inspect again curves 2 and 3 in Figs. 1a and b). This means that Cl^- is the aggressive ion that caused metastable pitting and not ClO_3^- and ClO_4^-. This may be due to the small size of Cl^- ion that allows it to occupy anion vacancies to initiate pitting corrosion according to the point defect model (PDM) [20].

(ii) In addition, the cooperative influence between Cl^- ions and either ClO_4^- or ClO_3^- anions is evident from the comparison between curves 2 and 3 in Figs. 1a and b; E_{pit} goes to a more negative value and j_{pass} enhances when Cl^- ions exist in solution.

(iii) Also, the images of SEM and AFM presented in Figs. 2 and 3 reflect the aggressive influence of both anions, even in absence of Cl^- (images c and d), as well as their collaboration with Cl^- ions in passivity rupture (images a and b). See more details in section 3.3.

3.3. Microstructural and topographical characterizations

The extent of corrosion damage caused by the aggressive attack of ClO_4^-, ClO_3^-, and Cl^- ions was assessed by microstructural and topographical characterizations of the pitted surfaces using SEM (Fig. 2) and AFM (Fig. 3) examinations. The pits in the SEM images are surrounded on all sides by the regions covered with oxide layer and corrosion products. On going from ClO_4^- (images a and c) to ClO_3^- (images b and d), the ratio of the pitted areas to total surface area (i.e., pit area density) increased, reflecting the intense pitting attack of ClO_3^- compared with that induced by ClO_4^-. The aggressive influence of ClO_4^- and ClO_3^- anions is quite evident, even in absence of Cl^- ions, see images (c and d).

AFM images came to the same conclusion, where rough surfaces were obtained, as expected from the aggressive attack of ClO_4^-, ClO_3^-, and Cl^-. To confirm these results, the mean roughness factor (R_a) was determined from the respective AFM images (Fig. 3). Obtained results showed that R_a values are always higher in presence of ClO_3^- (images b and d) as compared with ClO_4^- (images a and c).

4. CONCLUSIONS

Cathodic reduction of ClO_3^- and ClO_4^- to produce Cl^- ions and current oscillations (metastable pitting events) are employed to account for Zn passivity breakdown in NaOH solutions in presence of such anions. It is found that neither ClO_3^- nor ClO_4^- cause current oscillations. The origin of metastable pitting events is attributed to Cl^- ions. The obvious enhancement in current oscillations observed in the presence of ClO_3^- compared with ClO_4^- indicates an accelerated pitting attack. This is due to the faster reduction of ClO_3^- to form the aggressive Cl^- compared with that of ClO_4^-. However, experimental findings support that ClO_3^- and ClO_4^- anions cooperate with Cl^- to induce stable pitting. In addition, they are found to induce stable pitting even in absence of Cl^- ions, with ClO_3^- being more aggressive than ClO_4^-. The aggressive influence of Cl^- is explained on the basis of the PDM through the occupation of an oxygen vacancy by Cl^-. The local action induced by ClO_3^- and ClO_4^- could not be understood in terms of the PDM due to their large size with respect to that of the oxygen vacancy. SEM and AFM examinations confirmed passivity breakdown of Zn and initiation of pitting due to the aggressive influence of ClO_3^- and ClO_4^- in absence of Cl^-. Such microstructural and topographical characterizations also revealed that ClO_3^- and ClO_4^- anions contribute with chlorides in passivity breakdown and initiation of pitting.

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