

Localized Corrosion of Iron by Perchlorate
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Breakdown of Passivity and Localized Corrosion by halides is a well studied phenomenon and many investigations have been published to elucidate the various aspects to pit nucleation and pit growth. Pitting of iron by perchlorate is mentioned only briefly in literature although very characteristic observations could be mentioned. On one hand perchlorate acts as an inhibitor for halide pitting and inhibition potentials E_i have been found for mixtures of halides with perchlorate for iron and nickel which limit localized corrosion to positive potentials. E_i -values show a logarithmic dependence on the concentration ratio of the inhibiting and the aggressive anions. On the other hand perchlorate causes pitting at very positive potentials close to the values of oxygen evolution. $E_p = 1.46$ V has been found for the pitting potential in 1 M solutions of perchlorate in phthalate buffer pH 5.0 and borate buffer pH 9.3 and $E_p = 1.37$ V in 1 M HClO_4 . Its dependence on the concentration follows again a logarithmic relation, $E_p = 1.44 - 0.14 \lg [\text{ClO}_4^-]$. The pitting potential of perchlorate is almost pH independent and may be determined with a characteristically high accuracy of ± 4 mV when compared to critical potentials of other anions. For all pH values the shape of pits is very irregular. As a consequence the average local current density may be given as a rough estimate only, assuming a hemispherical shape as a first guess. In the early stages the local current densities are several 10 A/cm^2 with a steep increase with the potential. In later stages they are one order of magnitude smaller.

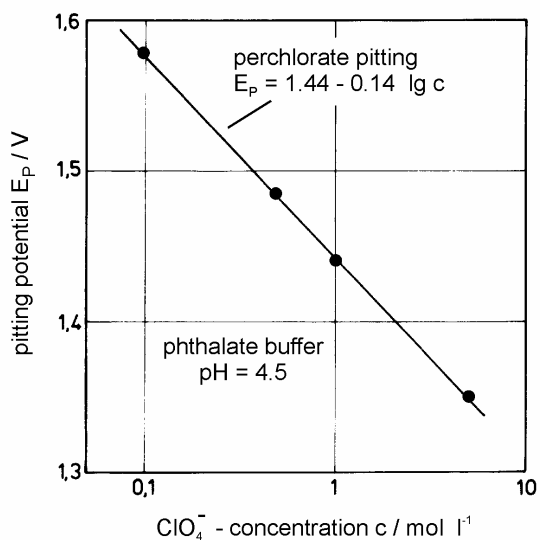


Fig. 1: Pitting Potential for perchlorate pitting as a function of the concentration c .

The main mechanism for pitting by halides refers to the complexing property of these anions to the cations in the surface of the passive layer, i.e. of Fe^{3+} -ions in the case of iron. The exchange of oxygen containing ligands by halides forms a surface complex which is easily transferred from the oxide matrix to the electrolyte. This increased transfer of cations will cause a thinning of the passive layer and finally breakdown of passivity. In the case of an already growing pit, the very high local current densities cause the local accumulation of corrosion products and thus of halides. Their high concentration

prevents the formation of a passive layer due to the increased formation of complexes. Perchlorate is very special in so far as no strong complexing properties exist as in the case of halides. As a consequence it acts as an inhibitor and not as an aggressive anion for lower potentials in the passive range. It is a general agreement that it is kinetically very stable so that it is not reduced to chloride even at very negative potentials. The standard potential of the $\text{ClO}_4^-/\text{Cl}^-$ electrode is 1.37 V. On the other hand pitting starts at potentials $E_p > 1.3$ V. A reasonable assumption is the decomposition of perchlorate at these potentials although this should not be seen as an electrochemical reduction which is not possible at potentials $E > 1.37$ V for thermodynamic reasons.

A possible explanation could be the decomposition of perchlorate to oxygen and chloride in the increasingly high electrical field at the interface of the passive layer and the electrolyte. In the transpassive range of the polarization curve the potential increase is located at this interface. To get experimental evidence of this effect the formation of chloride has been followed with XPS on emersed passivated iron electrodes after pitting by perchlorate. An increasing amount of chloride has been found in addition to perchlorate. The decomposition of perchlorate due to the irradiation by X-rays during XPS analysis is negligibly small and could be excluded as an explanation for these findings. Similarly its reduction within the electrolyte by Fe^{2+} -ions, which form within corroding pits, could be excluded by appropriate tests in solution. One therefore has to conclude that chloride is formed at the electrode surface by decomposition of perchlorate within the very high electrical field of the passive layer/electrolyte interface. This chloride acts as usual as an aggressive anion causing pitting.

To confirm this interpretation the influence of ClO_3^- on passive iron has been studied. Chlorate causes breakdown passivity and localized corrosion at any pH as i.e. 0.5 M H_2SO_4 , phthalate buffer pH 5.0 and borate buffer pH 9.3. In borate buffer pH 9.3 with 0.01 M NaClO_3 a critical pitting potential of $E_p = 0.20$ V has been determined by galvanostatic and potentiostatic experiments. Only a few pits were formed and the local pit current density was relatively small, i.e. ca. 120 mA/cm^2 . In both chlorate containing acidic solutions, i.e. phthalate buffer pH 5.0 and 0.5 M H_2SO_4 , serious pitting has been found. Local current densities of several 10 A/cm^2 have been measured for both electrolytes. It is interesting, that pitting in borate buffer by chlorate stops above $E_i = 0.76$ V. This is not far from the standard potential of the $\text{ClO}_3^-/\text{Cl}^-$ electrode for pH 9.3 of 0.90 V. Apparently the ClO_3^- -reduction is no longer effective for $E > E_i$ so that no chloride has access to the iron surface which stops pitting.

The various details for pitting by chlorate and perchlorate suggest the decomposition of these anions and the formation of chloride as a start for breakdown passivity and localized corrosion. For chlorate the reduction to chloride at the electrode surface is a reasonable assumption. However, perchlorate is kinetically very stable and may not be reduced at negative potentials. Therefore it acts as an inhibitor rather than an aggressive anion. On the contrary it causes pitting at potentials above the $\text{ClO}_4^-/\text{Cl}^-$ redox potential. Nevertheless chloride formation at the electrode surface has been detected. Therefore not the electrochemical reduction but the decomposition of the perchlorate anions in the high field of the passive layer/electrolyte interface is proposed. In any case chloride is formed first and causes breakdown of passivity and localized corrosion as a consequence.