Surface Reactions on Metal and Associated Impact of Salt Anions

In an oxygen rich environment:
[1] $2Fe + 2H_2O + O_2 \rightarrow 2Fe(OH)_2$ or hydrous ferrous oxide ($FeO \cdot nH_2O$) forming closest to the surface. pH of saturated $Fe(OH)_2$ is ~9.5 and has a greenish blue color.
[2] $4Fe(OH)_2 + 2H_2O + O_2 \rightarrow 4Fe(OH)_3$
[1] and [2] are commonly called passivation reactions.

In crevices, O_2 deficiency exists in the anodic region. In the pits and crevices, the ***presence of Cl^- ions*** favor hydration of metal ions and increase the ease with which the metal ions enter into solution. Cl^- ions present will migrate to the pit to maintain electroneutrality. The consequence of this stabilization is increased pitting susceptibility caused by the increased concentration of the pit solution.
At the bottom of the anode:
[3} $Fe \rightarrow Fe^{+2} + 2e^-$ Anodic oxidation. Energy is released. The metal goes into solution at the anode in equivalent amounts to the cathode reaction.
In the presence of moisture in the anodic area, hydrolysis takes place in the pits:
[4] $Fe^{+2} + H_2O \rightarrow Fe(OH)^+ + H^+$ {H^+ concentration can increase due to confined spaces}
Repassivation is prevented by a high enough concentration of Cl^-, which would be the case in an oxygen rich environment.
[5] $Fe + 2H^+ \rightarrow Fe^{+2} + H_2\uparrow$ From the H^+ in [4] {The subject of hydrogen gas produced is argued.} These are acidic cathodic reactions which follow from [3] because of hydrolysis in the crevice or pit. pH of 2.4 or less has been measured for these solutions.

At the cathode, Electrons from the anodic oxidation migrate through the conductive metal to the cathode {cathodic reduction}:
[6] $4e^- + O_2 + 2H_2O \rightarrow 4OH^-$ {In neutral environments}
    [6a] $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ {In acidic environments, as in the case where pits present}
    [6b] $2H^+ + 2e^- \rightarrow H_2$
[7] $Na^+ + OH^- \rightarrow NaOH$ {From Na^+ cations associated with Cl^- anion.}
A ***passivation*** ring around the pit is formed. The tested pH of the surface in solution is alkaline, which is the reason pitting is localized. {Note: The cationic species is important in determining the size and distance from the pit.}

Passivation on the surface, resulting in substantial resistance to corrosion, can be attributed to reactions in [1] and [2] with the development of an initial passive film growing into a multilayer adsorbed structure. Oxygen present helps transition the passivation in alkaline or near neutral solutions. The ferrous form (Fe^{+2}) oxidizes to the ferric form (Fe^{+3}) due to greater stability of the ferric ion. $Fe(OH)_3$ is also $Fe_2O_3 \cdot 3H_2O$, which is red brown in color. A magnetic ferrous ferrite, $Fe_3O_4 \cdot nH_2O$ forms between the FeO and the Fe_2O_3. A high energy of adsorption of oxygen on transition metals corresponds to chemical-bond formation.

In the pits or crevices:
[8] $Fe^{+2} + 2Cl^- \rightarrow FeCl_2$ From [5] in the presence of Cl^-. { $FeCl_2$ defined as an acid salt.}

Formation of metal ion solution is drawn to the surface, seeking pH neutrality:
[10] $2FeCl_2 + O_2 \rightarrow 2FeO + 4Cl^-$ {Adsorbed oxygen decreases the rate of metal dissolution.}
Or, can be shown as [4]. *([10] not balanced to reflect that the Cl^- ion is still present.)*
The oxide moves to the surface to become part of the passivation barrier layer.
The ***continuing presence of the Cl^- ion*** in the acidic anodic reaction environment [5] increases the ease with which the metal ion enters into solution.

In summary, hydrolysis in the oxygen deficient pits and crevices, along with the presence of a Cl^- salt anion increases the ease for the metal ion to enter into solution. To the contrary, in the oxygen rich environment of the cathodic surface, moisture and oxygen generate passivating hydroxide and oxides of the metal.

Diagram of Reactions