

The Role of Chloride Ion in Passivity Breakdown on Nickel and Chromium

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Corrosion, including localized corrosion, such as pitting attack and stress corrosion cracking, is estimated to cost an industrialized nation more than 4 % of the GNP annually (approximately \$ 400 billion for the U.S. in 2002), rendering it one of the most important costs in operating industrial systems. However, in spite of numerous studies on the mechanism of initial passivity breakdown, considerable controversy exists as to the exact nature of the processes involved at the atomic scale. In this communication, we assess the impact that chloride ion, which is known to induce passivity breakdown on many metals and alloys, has on the electronic and point defect structures of the passive state on nickel and chromium (Figure 1). We show by Mott-Schottky analysis that, as the concentration of Cl^- in pH 8.5 borate buffer solution increases, the concentration of metal vacancies ($V_M^{\chi'}$) in the passive film on Ni also increases (Figure 2). The addition of Cl^- to pH 8.5 borate buffer solution after passivity has been established in the absence of Cl^- also results in an increase in the concentration of metal vacancies ($V_{\text{Ni}}^{\chi'}$) in the passive film. Finally, by using electrochemical impedance spectroscopy to interrogate the point defect generation and annihilation reactions that occur at the metal/film and film/solution interfaces, we show that the observed increase in cation vacancy concentration in the passive film is due to chloride catalyzed ejection of cations from the film/solution interface (Figure 3). These findings are inconsistent with chloride-catalyzed film dissolution and chloride penetration mechanisms for passivity breakdown, but they are consistent with the Point Defect Model.

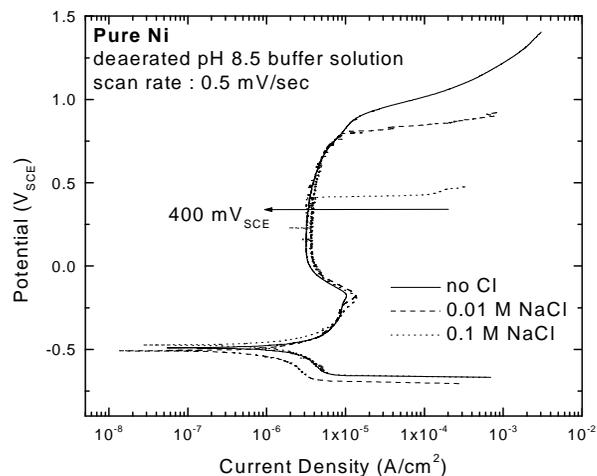


Figure 1. Polarization curves for nickel in borate buffer solution as a function of chloride concentration.

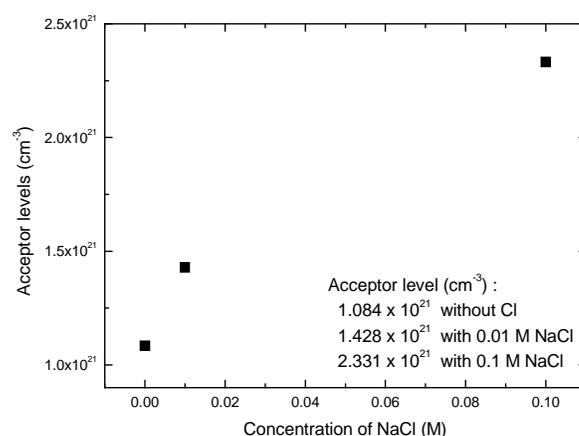


Figure 2. Cation vacancy concentration in the passive film on nickel as a function of chloride concentration.

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