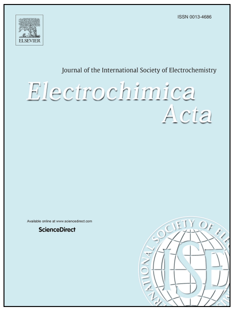

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Oxidation versus salt-film formation: Competitive adsorption on a series of metals from first-principles

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Abstract

Chloride ion is known to accelerate corrosion in numerous metallic systems, although it is not well understood why. Using first-principles methods, such as density functional theory, it is possible to directly compute the energy of adsorption for chloride, and using a thermodynamic framework based on statistical mechanics, to predict the environmental conditions under which it may be anticipated that chloride could displace other ions (such as hydroxide, incipient oxide, or other potentially corrosion inhibiting species) from the bare metal and/or oxide surface. By reviewing the literature, as well as performing some original density functional theory calculations, the authors present in this work the dependence of the surface coverage for H_2O, OH, O and Cl on the electrochemical potential, pH and chloride concentration for a number of metallic systems, including nickel, iron, magnesium and aluminum, to predict the fundamental surface processes that may related to the role of chloride in potentially interfering with processes such as repassivation and metal dissolution. It is found that under some conditions certain metals can possess zones of mutual stability where both chloride and hydroxide may be coadsorbed, whereas other metals appear to have intrinsic resistance to chloride adsorption. Variations among the available first-principles adsorption energies obtained from different sources indicates that uncertainty analysis is necessary moving forwards. An analogous approach could be taken to consider the interaction of chloride with clean and defective oxide and/or hydroxylated surfaces.

Key words: Localized corrosion, adsorption, chemisorption, chloride, water, pre-passivation, modeling

Introduction

Localized corrosion processes involve the undermining of passivity through chemical or mechanical means, directly exposing the underlying metal to the chemical environment, whereby dissolution is accelerated, and can outpace the process of repassivation. Metastable pits suffer from initial attack due to the breach of passivity, but then recover when repassivation 'heals' the exposed metal surface.[1] A metastable pit can 'survive' this phase if an aggressive pit chemistry develops that favors the continuation of the corrosion processes and hinders the repassivation process.[2] It is not yet well understood what these circumstances are. However, the model developed by Anderko, Sridhar and Dunn provides a foundational understanding through the competing forces of adsorption of environmental species that can either inhibit corrosion and encourage the growth of passivating oxide phases or accelerate corrosion, by acting as ligands/complexation agents.[3-5]

To begin to shed light on those competing forces, the current paper proposes a method to utilize fundamental data made available through first-principles density functional theory calculations to predict under what conditions either Cl, H_2O, OH or O will dominate the surface coverage of an exposed metallic surface. While this model does not provide a complete mechanistic picture for pit growth vs repassivation, it can provide something analogous to a Pourbaix diagram for the metallic surface.[6] The work, in fact, bears strong similarity to the concept of a surface Pourbaix diagram as developed by Marcus and Protopopoff,[7] and also by Taylor and co-workers,[8-10] and Williams et al.[11] Where it extends the state of the art is through linkage to a multi-adsorption model that predicts fractional surface coverage using a Langmuir isotherm.