
Atomic insights into the Cl⁻-induced passivity breakdown on iron and iron-base alloys

Dihao Chen, Chaofang Dong*

Beijing Advanced Innovation Center for Materials Genome Engineering, Key Laboratory for Corrosion and Protection (MOE), Institute for Advanced Materials and Technology, University of Science and Technology Beijing, Beijing 100083, PR China

dhchen@xs.ustb.edu.cn

Abstract Understanding towards mechanism of passivity breakdown and pitting for metals is always a matter of interest to corrosion scientists. Herein, an atomic model based on the point defect model is developed, in which the fundamental processes of Cl⁻ hydration, Cl⁻ adsorption, Cl⁻ insertion, dissolution of metal cation and pit initiation are considered. This model quantitatively reveals a relation between the amount adsorbed Cl⁻ on passive film and Cl⁻ concentration in electrolyte as well as applied potential. It shows that (i) pitting potential decreases linearly with the increasing logarithm of Cl⁻ concentration, (ii) pitting potential linearly depends on pH of solution, and (iii) pitting potential drops linearly with the rising temperature. Moreover, it predicts the linear decrease of logarithm of incubation time of pitting with the increasing applied potential and with the logarithm of Cl⁻ concentration. It also demonstrates that the critical pitting temperature (CPT) linearly reduces with the increasing applied potential, and that the inverse of CPT linearly increases with the logarithm of Cl⁻ concentration. Moreover, the size effects of F⁻, Cl⁻, Br⁻ and I⁻ on pitting are concerned. The experiment results for iron and iron-base alloys, and first-principles calculations results well support above theoretical predictions and findings. It theoretically provides enlightenment for the corrosion-resistant alloys design from the perspective of modifying properties of passive film.

Keywords Passivity breakdown; Pitting; Point Defect Model