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Elucidating the Role of Electric Fields in Fe Oxidation via Operando Atom Probe

Abstract

We quantify the effects of intensely applied electric fields on the surface Fe oxidation mechanism. The specimen are pristine Fe nanocrystals exposing a variety of surface structures identified by Field Ion Microscopy. These crystals are simultaneously exposed to low pressures of pure oxygen gas, on the order of 10^{-7} mbar, while applying intense electric fields on their surface of several tens of volts per nanometer. The local composition of the different surface structures is probed directly and in real time using Operando Atom Probe and successfully compared with first principles-based models. We found that rough Fe₂₄₄ and Fe₁₁₂ facets are more reactive towards oxygen than compact Fe₀₂₄ and Fe₀₁₁ facets. Results demonstrate that the influence of an electric field on the oxidation kinetics depends on the timescales that are involved as the system evolves toward equilibrium. The initial oxidation kinetics show that strong increases in electric fields facilitate the formation of an oxide. However, as one approaches equilibrium, high field values mitigate this formation.