

Oxidation of the Copper (100) Surface Induced by Local Alkalization

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Motivation—It is generally known that the stability of metal surfaces can be greatly influenced by *localized phenomena* associated with the oxygen reduction reaction (ORR). The ORR is considered as one of the most important electrochemical reactions in the field of corrosion. The kinetics of the ORR processes often determines the general corrosion rate of metals and the damage evolution in many commercially important alloys. As the ORR proceeds on the copper surface, by either consuming hydrogen ions or generating hydroxide ions, the local pH can increase well above the solution bulk value, setting a pH gradient from the surface toward the bulk of the solution. Therefore, the ideal conditions for the oxidation to take place are created locally, even in acidic aqueous media for which the equilibrium thermodynamics rule out the possibility of stable oxide formation.

Accomplishment—Our work presents the first *in-situ* scanning tunneling microscopy (STM) study of the initial stages of Cu(100) oxidation occurring in *naturally aerated acidic solutions*. The presence of dissolved oxygen in the solution results in a very distinctive electrochemical behavior of the Cu(100) surface that is manifested by pairs of pronounced peaks not present in deaerated solutions with identical pH, Fig. 1. The observed difference is a clear manifestation of the kinetic effect of the ORR that results in local solution alkalization. The set of peaks observed in naturally aerated solutions represent the adsorption/oxidation surface processes taking place, while their pH-dependent behavior points toward the important role of oxygen species (O and OH⁻) in the

process of surface oxide formation. Following the surface structures and morphological changes using an *in-situ* STM, we showed how the extent of local alkalization and the concomitant extent of oxidation depend on experimental conditions: solution pH, potential and time of exposure. We focused our research on the initial stages of copper oxidation, known as underpotential oxidation, in a 0.1 M NaClO₄ solution of pH 2 and pH 4, Fig. 2. Quantitative analysis showed that in highly acidic solutions (pH 2), the surface actually experiences much higher pH of almost 7 to 8. *In-situ* STM results in pH 4 solutions revealed a striking similarity with the morphologies usually observed in alkaline solutions of pH 9 to 11. These results confirm the proposed local alkalization mechanism governing the stability of the copper surface.

Significance—In recent years copper surface stability became an increasingly important issue due to its varied applications in many fields of technological importance. Our knowledge of locally-induced copper oxidation will impact the technology of copper processing and design procedures in the electronics industry, help in understanding the corrosion behavior of copper-based alloys and eventually help in improving their corrosion resistance. This work provides an opportunity to generate a new body of knowledge that will enable development of many pH-controlled processes, playing a key role in the fields of solid-state synthesis, corrosion and chemical sensing. From the fundamental point of view, our work opens new pathways in studying and understanding the initial stages of noble metal oxidation.

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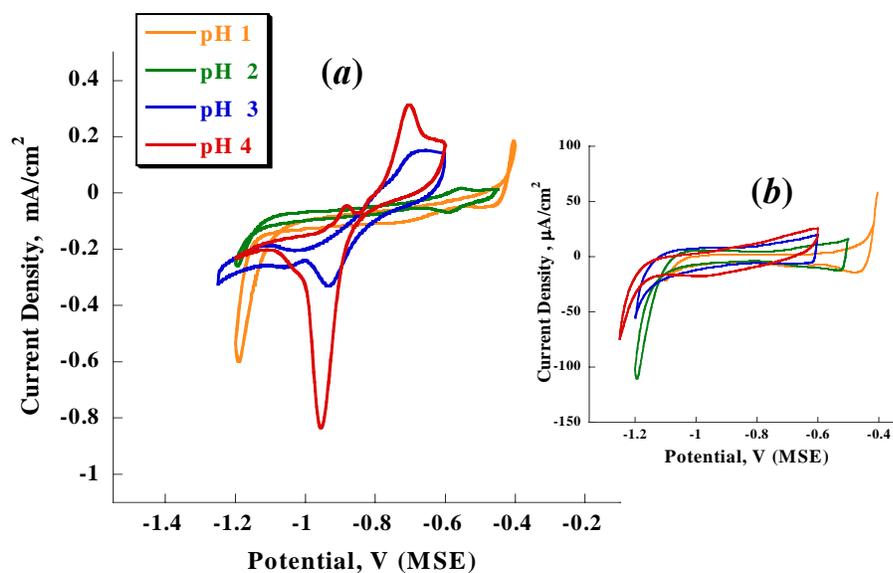


Figure 1. Cyclic voltammeteries of Cu(100) in 0.1 M NaClO₄ solutions of different pH with a scan rate of 150 mV/s. (a) Naturally aerated and (b) deaerated solutions.

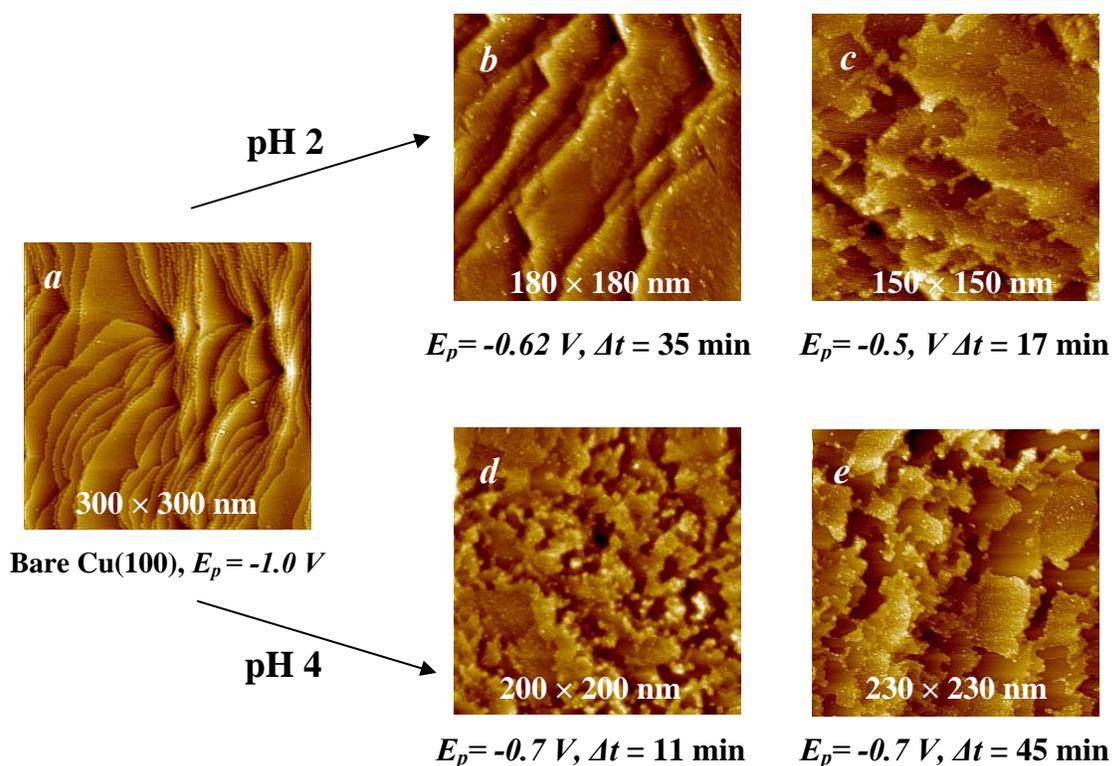


Figure 2. *In-situ* STM images of the Cu(100) surface at different potentials in 0.1 M NaClO₄ solutions of pH 2 and pH 4. (a) Bare surface. Potential dependant surface processes: (b) oxygen adsorption and (c) monolayer of underpotential Cu₂O growth in solution pH 2. (d) Underpotential and (e) bulk growth of Cu₂O in pH 4 solution.