

Effects of chlorides on the growth mechanism and structure of passive films on copper

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The effect of chlorides on the anodic oxidation of Cu(111) in alkaline NaOH solutions has been studied by Electrochemical Scanning Tunneling Microscopy (ECSTM) for  $[Cl^-]/[OH^-]$  concentration ratios of 0.01, 0.1 and 10.

Three different electrolytes were used : (i)  $10^{-1}$  M NaOH +  $10^{-3}$  M NaCl (pH 13), (ii)  $10^{-1}$  M NaOH +  $10^{-2}$  M NaCl (pH 13) and (iii)  $10^{-3}$  M NaOH +  $10^{-2}$  M NaCl (pH 11). They were prepared from ultra pure chemicals (Gen-Apex) and Millipore water (resistivity > 18 M $\Omega$ cm).

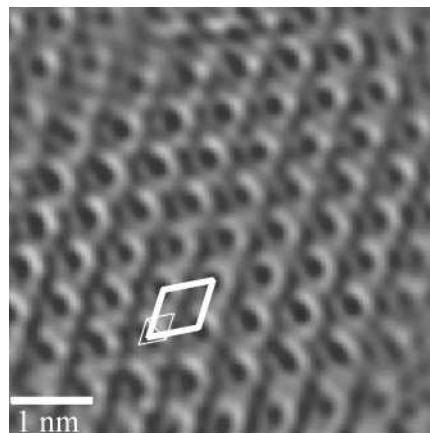
The Cu(111) single-crystals were produced from a single-crystal rod oriented by Laue diffraction with a precision of  $1^\circ$  and cut by spark erosion. The surface was mechanically polished with diamond spray with a final 0.25  $\mu$ m grading. The samples were then electropolished and subsequently annealed at about 1000 K in a flow of ultra pure hydrogen at atmospheric pressure. They were mounted in a small electrochemical cell of the STM with a surface of 0.16 cm<sup>2</sup> exposed to the electrolyte. The electrode surface was exposed to the electrolyte at open circuit potential and reduced cathodically at -1.2 V/SHE to remove the air-formed oxide film. After this pretreatment, the potential was stepped to the value of interest.

The ECSTM observations were performed with a Molecular Imaging PicoSPM. Tips were produced from a W wire by electrochemical etching and covered by apiezon wax. All images were obtained in the constant current mode.

The ECSTM results show that the ordered OH adsorption structure, previously observed in Cl<sup>-</sup>-free NaOH in the underpotential range of oxidation<sup>1</sup>, also forms in the presence of chlorides. Atomically-resolved images (see figure) evidence the reconstruction of the topmost Cu plane into a less densely packed hexagonal structure and the adsorption of hydroxide in the threefold hollow sites of this structure to form a precursor surface layer adopting the structure of (111)-oriented Cu<sub>2</sub>O.

At low chloride concentrations, no influence of Cl<sup>-</sup> on the growth of the OH adlayer is found. For increasing chloride contents, a competition between chloride and OH adsorption is observed at step edges, where copper atoms are mobile. The adsorption of hydroxides is still dominating at the step edges by forming an OH adsorption structure expanding across the terraces with increasing potential and for longer times. Copper atoms, ejected from the metallic surface by the reconstruction, are revealed after reaction with the chlorides due to their reduced surface mobility. They form temporary threadlike nanostructures which are assigned to chloride containing copper species. These nanostructures are no longer observed in the final stages of the adsorption process due to their agglomeration with

the 2D Cu ad-islands formed by the ejected copper atoms, less mobile on the OH-covered surface.



Topographic ECSTM image of Cu(111) in  $10^{-1}$  M NaOH +  $10^{-2}$  M NaCl at -0.58 V/SHE, showing the ordered superstructure of the OH adlayer (bold line) and the reconstructed copper unit cell (thin line).

At higher Cl<sup>-</sup> concentration, the preferential reaction of hydroxides at the step edges of the copper surface is fully blocked by the formation of non-ordered copper chloride compound, but still dominates in the center of terraces. 2D ad-islands are formed much earlier during the adsorption process due to the reconstruction of the topmost copper plane. This is assigned to the blocking character of Cl<sup>-</sup> at step edges that prevents copper accumulation and the resulting lateral growth of the terraces at these sites. A faster capture of the ejected Cu atoms by Cl<sup>-</sup> before reaching and reacting with the step edges is also suggested. Threadlike nanostructures are no longer observed for these conditions.

The presence of chlorides does not modify significantly the structural characteristics of the Cu(I) oxide layer. A highly stepped and (111)-oriented crystalline Cu<sub>2</sub>O layer is formed as in Cl<sup>-</sup>-free NaOH, the step edges of which are rougher and indented in comparison to the situation in absence of chloride. This is assigned to an enhanced localized Cu-dissolution at the oxide step edges in the presence of chlorides.

These results show that although the adsorption process leading to the growth of anodic oxide layers on Cu(111) can be modified by the presence of chlorides, the reaction with hydroxides dominates the surface reactivity in the potential range of oxidation to Cu(I) for  $[Cl^-]/[OH^-]$  concentration ratios ranging from 0.01 to 10 in alkaline electrolytes (pH $\geq$ 11).

1. V. Maurice, H.-H. Strehblow, P. Marcus, *Surface Sci.* **458** (2000) 185.