

The potential dependence of coarsening phenomena at the metal/electrolyte interfaces

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During the last few years new methods have been developed by which defect formation energies and activation energies for defect migration can be determined not only for surfaces in vacuum but also for surfaces in contact with an electrolyte, which has added novel, quantitative aspects to electrochemistry. To a large extent the work was initiated by Giesen et al. and has been reviewed in [1]. An example of this work is the recent determination of the step line tension and its dependence on the electrode potential using a method which is based on the observation of shape fluctuations of islands [2-4]. Furthermore it was found that the potential dependence of the magnitude of step fluctuations and of the speed of coarsening processes can frequently be described by an ansatz which assumes a linear potential dependence of the activation energies involved in the fluctuations (Fig.1 and 2) [5, 6].

Stimulated by these experimental achievements we have investigated theoretically the nature of the step line tension for metals in contact with an electrolyte, and we presented the first model calculation on the step line tension and its dependence on the electrode potential which considers the metal and the electrolyte simultaneously [7, 8]. We find that (in the absence of specific adsorption) the dominant contribution to the potential dependence of the line tension arises from the energy of the step dipole moment in the electric field of the double layer. To first order, this gives rise to a linear dependence of the line tension on the electrode potential.

In this work we show that the arguments can be generalized to other defect energies as well as to activation energies for diffusion and coarsening processes. According to these arguments the slope of the linear dependence of the energies of formation of an adatom or a vacancy from a kink site is determined by the dipole moment of the defect. The potential dependence of the activation energy for diffusion is determined by the difference in the dipole moments in the transition state and the ground state. In order to investigate the quantitative aspects of the model, we have calculated defect energies, activation energies for migration and the dipole moments for a number of configuration on the (100) and (111) surfaces of Au, Ag, and Cu. The results will be compared to the available experimental data.

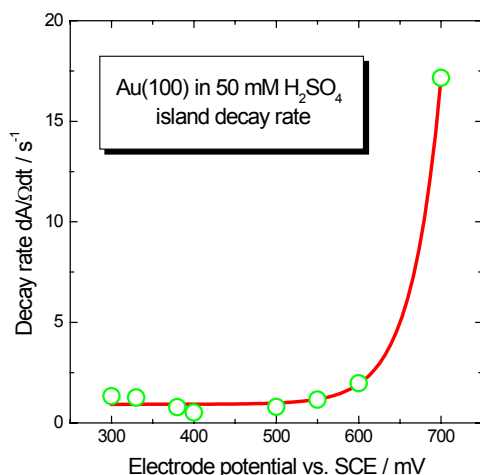


Fig. 1 Decay rate of an island in atoms per second of an Au(100) surface in 50 mM H₂SO₄ as a function of the electrode potential vs. a saturated calomel electrode (SCE) [5]. The potential range shown is positive with respect to the potential of zero charge (pzc) in which the unreconstructed surface is stable. The island are produced by the lifting of the reconstruction of the gold surface.

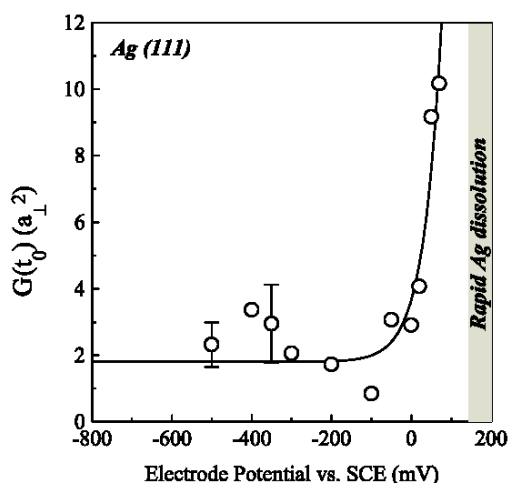


Fig. 2: Step fluctuations on an Ag(111) surface measured as the mean square deviation of the step position during a time span of 11s as a function of the potential [1,6].

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