Chlorine-enhanced surface mobility of Au(100)

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Motivated by experimental studies of two-dimensional Ostwald ripening on Au(100) electrodes in chlorine containing electrolytes we have studied diffusion processes using density functional theory. We find that chlorine has a propensity to temporary form AuCl complexes which diffuse significantly faster than Au adatoms. With and without chlorine, the lowest activation energy is found for the exchange mechanism. Chlorine also reduces the activation energy for the detachment from kink sites. Kinetic Monte Carlos simulations were performed on the basis of extensive DFT calculations. The island decay rate obtained from these Monte Carlo simulations as well as the decay rate obtained from the theoretical activation energies and the theoretical frequency factors when inserted into analytical solutions for Ostwald ripening are in excellent agreement with experimental island decay rates in chlorine-containing electrolytes.

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Surface diffusion plays an important role in non-equilibrium phenomena such as catalyst degradation, corrosion, faceting, sintering, and annealing. In all cases, the driving force for diffusion is the minimization of the surface free energy. An atomic view on mass transport on surfaces must take into account a large number of individual processes and it is not always clear a priori which one is rate-determining. A rather transparent case is two-dimensional Ostwald ripening in which large islands of one layer height grow at the expense of smaller ones. In this case, two atomic processes are rate-determining, the detachment from a kink site and the diffusion on the flat surface between the islands. Therefore, many quantitative experimental and theoretical studies have been devoted to studies of this geometry (for a review see [1]). Most of these studies concerned surfaces in ultra-high vacuum; however surface diffusion is just as important in electrochemical systems, in which the electrode potential is an additional variable that controls the speed of diffusion processes. A number of studies have shown, that the surface mobility typically increases when the potential is scanned towards higher potentials [1]. Two mechanisms seem to operate: One is based on the interaction of the double-layer field with the local dipole moment of adatoms and steps [2-4]; this interaction gives rise to a roughly exponential increase of step fluctuations and island decay rates in Ostwald ripening [2]. The effect has recently been investigated theoretically on silver surfaces and applied to the mobility on silver surfaces [5, 6]. Surface mobility is also enhanced by adsorbates which reduce the activation energies for transport. For example, it has been shown that the adsorption of chlorine greatly enhances the surface mobility on Gold surfaces in an electrolyte [7, 8]. The facilitation of diffusion on surfaces in vacuum by adsorbates been studied experimentally and theoretically [9-12].

These observations have motivated us to investigate the effect of chlorine adsorption on Ostwald ripening on Au(100) surfaces. Since diffusion on terraces is a crucial step in Ostwald ripening, we firstly focus on the question as to whether and how chlorine may facilitate diffusion on terraces.

We begin with the diffusion of gold atoms on flat Au(100) surfaces without the presence of chlorine. All calculations are performed on the unreconstructed surface since experimental data were obtained at electrode potentials where the reconstruction is lifted. Two mechanisms can be distinguished: hopping of adatoms between adjacent adsorption sites and transport of an atom via exchange between adatoms and substrate atoms (see ref. [13] and citations therein). Density functional theory (DFT) calculations have demonstrated that the hopping mechanism is preferred for (100) surfaces of late 4d metals (e.g., Rh [14], Ag [15], and Pd [16]), while the exchange mechanism dominates on (100) surfaces of late 3d (e.g., Ni [17]) and 5d metals (e.g. Ir [18], Pt [19], and Au [20]).

Our DFT calculations were performed with SeqQuest [21] employing localized basis sets represented by a linear combination of optimized double-ζ plus polarization-contracted Gaussian functions. Effects of Au core electrons were replaced by norm-conserving pseudopotentials, including nonlinear core corrections. The PBE flavor [22] of generalized gradient approximation (GGA) was used as exchange correlation potential. Convergence in binding energies was obtained with a (i) (5x5) unit cell; (ii) Monkhorst-Pack *k*-point mesh of 2x2; and (iii) six-layer slab. Geometry optimizations have been performed for all atoms except the two bottom layers (up to 0.01 eV/Å).

Not unexpected, we find that the site of lowest energy for adatoms is the fourfold hollow site for which we calculate a binding energy of E_b=0.45eV with reference to the bulk energy which is equivalent to the binding energy of an atom residing in a kink site.

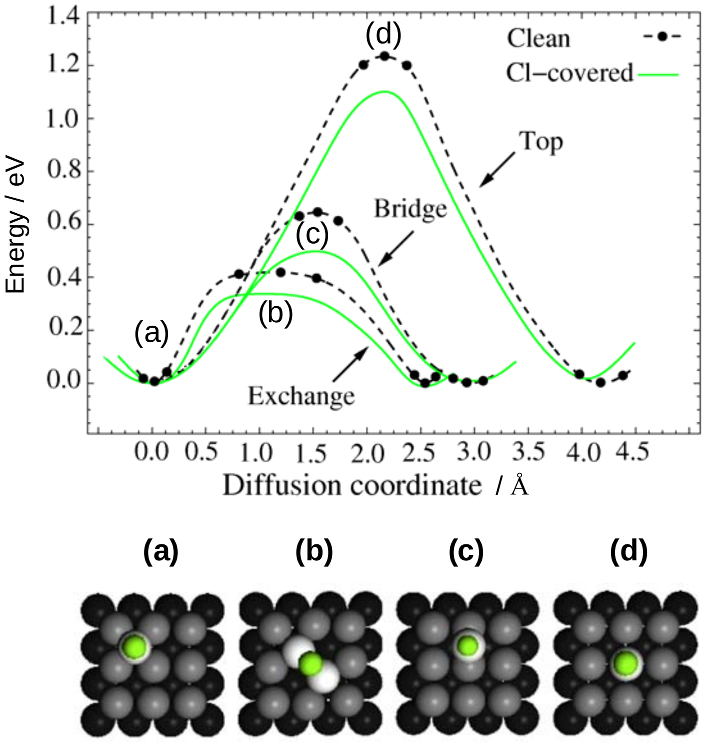

FIG. 1: Energy profile for diffusion on Au(100) for hopping via bridge and top sites and for the exchange process. Solid green lines and dashed, black lines (color online) are for adatoms with and without chlorine decoration, respectively. The ball models show the top views of initial, transition, and final states.

The corresponding values for bridge and top sites are higher, leading to substantial energy barriers for diffusion across these sites. In agreement with previous DFT calculations [15, 23] we find that adatom diffusion on Au(100) via the exchange mechanism (activation barrier of 0.42 eV) possesses a lower activation energy than hopping processes (see Fig. 1). Preference for exchange diffusion in the case of Au(100) surfaces was also found in cluster calculations [4].

Since there is no evidence for absorption of Cl atoms into the Au surface [24, 25], only adsorption on the surface is considered. Our calculations for the on-surface adsorption of Cl at low coverage (Θ = 1/25) show that the bridge site with a binding energy of 1.30eV, referenced to 1/2 Cl_2, is more stable than hollow or top sites by 0.11eV and 0.30eV, respectively. As the diffusing species in the case of chlorine adsorption we propose Au adatoms with a chlorine atom on top. The binding energy of Cl on top of Au adatoms is larger than the binding energy on the terrace but by a very small amount of 0.03 eV. This difference is within the errors of DFT. Regardless whether the binding energy of chlorine on top of a gold atom is slightly less or larger than the binding energy on a terrace one can conclude that for any finite coverage of the surface with chlorine a considerable fraction of adatoms should carry a Cl atom on top. Starting with an Au adatom at a hollow site, the diffusion barriers for various hopping and exchange processes have been calculated. It is found that a Cl atom on top of an Au adatom decreases the energy barriers for all three mechanisms, via top, via bridge, and exchange (see Fig.1). Again the exchange mechanism has the lowest activation barrier. In the transition state for exchange diffusion, the Cl atom sits at the bridge site offered by the adatom and the uplifted surface atoms (see Fig. 1). This is in line with the preference of Cl to occupy bridge sites on the bare Au(100) surface. The lower activation energies for diffusion of the ClAu complex is caused by the strong bonding of the Cl 3p orbitals to the Au 5d orbitals while the bonding of the gold atom to the substrate is somewhat weakened.

In order to have an approximation for the pre-exponential factors k_0 in diffusion we calculated vibration frequencies of the adatom complexes along the paths of the various diffusion processes using the harmonic approximation. As can be seen from Table I, the frequencies k_0 have the typical order of magnitude of 10^{12} s^{-1}. Compared to both hopping pathways the prefactor is higher for the exchange process. The effect is enhanced by the presence of Cl. The corresponding diffusion rates $k=k_0\exp(-\Delta E/k_B T)$ for 300K are likewise listed in Table 1. In total our calculations predict that gold diffusion is 30 times faster in the presence of chlorine.

		Au(100)			**Cl/Au(100)**	
pathway	**ΔE/eV**	**k_0/s^{-1}**	**k/s^{-1}**	**ΔE/eV**	**k_0/s^{-1}**	**k/s^{-1}**
via top	1.23	$1.35\text{x}10^{12}$	$2.93\text{x}10^{-9}$	1.10	$9.9\text{x}10^{11}$	$4.83\text{x}10^{-7}$
via bridge	0.64	$1.38\text{x}10^{12}$	2.44	0.50	$9.9\text{x}10^{11}$	$5.80\text{x}10^{3}$
exchange	0.42	$2.55\text{x}10^{12}$	$2.24\text{x}10^{5}$	0.34	$3.2\text{x}10^{12}$	$6.23\text{x}10^{6}$

TABLE I: Activation energies for diffusion ΔE, prefactors k_0 and rate constants k at 300K for Au adatoms and ClAu complexes.

For two-dimensional Ostwald ripening the detachment of an atom from a kink site onto the terrace is a crucial step. Fig. 2 shows the corresponding energy profiles, both in absence and in presence of Cl. Here, the lowering of the barrier by the presence of Cl is even larger (ca.

0.35 eV) than for diffusion on the terrace. We note the binding energy of a gold atom decorated with a chlorine atom with reference to a kink site decorated with chlorine is also reduced to E_b=0.39eV compared to the case without chlorine.

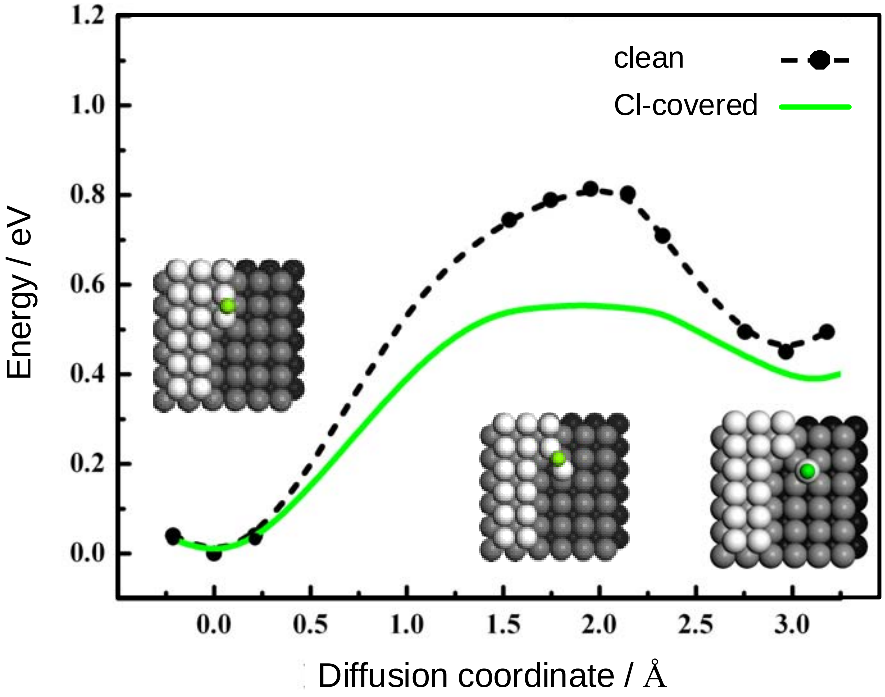

FIG. 2: Energy profile for the detachment of a gold atom from a kink site. The ball models show top views of initial, transition, and final state.

In order to investigate the effect of chlorine on Ostwald ripening, we have performed kinetic Monte Carlo simulations. For this purpose, we used the DFT results for 16 selected processes to train a force-field, from which we calculated the rates of all relevant processes. The method employed is the same as in [6]; details will be published elsewhere. Following [6], we investigated the Ostwald ripening of an island, which initially contained 218 atoms, situated in the centre of a vacancy island of 75x75 atoms. In the absence of adsorbed Cl, the island was stable over the time of 1000s (solid line in Fig. 3). In the presence of chlorine, the island decayed completely (dashed line in Fig. 3). The results agree well with experimental observations of island decay in 100mM $HClO_4$ electrolyte with and without 1mM HCl added (squares and circles in Fig. 3, respectively).

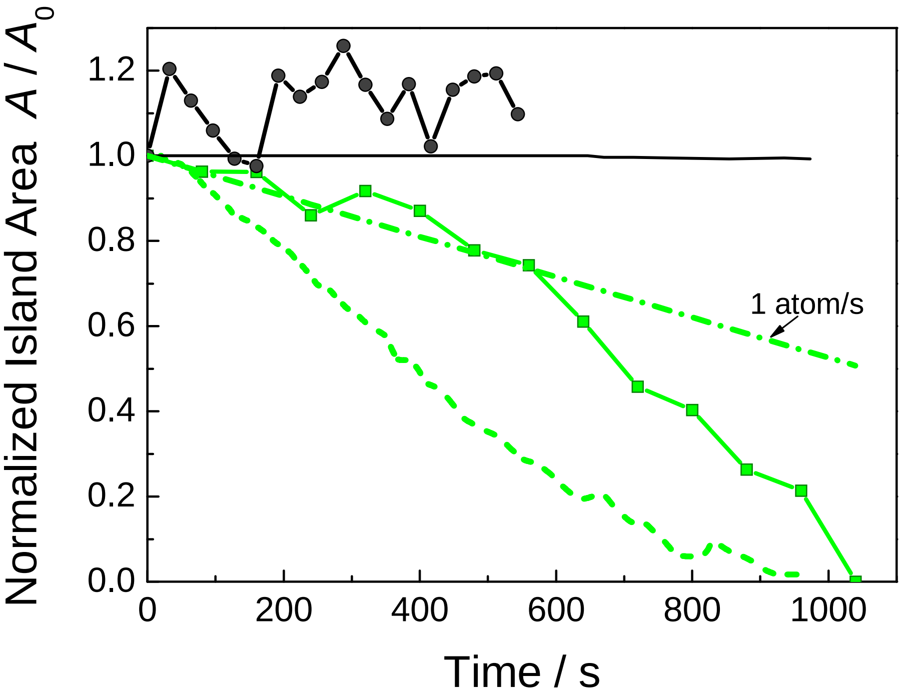

Fig. 3: Comparison of the kinetic Monte Carlo simulation and experiments on the decay of inlands on Au(100) surfaces. Solid and dashed lines are simulations without and with chlorine, respectively. Solid circles and squares are the experimental results without and with chlorine added to the electrolyte. Island areas are normalized to their initial size. the dashed dotted line shows approximately the initial rate of decay for the experimental island of the size of 2100 atoms.

Despite the pleasing agreement in the general trend there is characteristic difference between simulations and experiment: The simulated island decays roughly linear in time whereas the experimentally observed decay rate increases as the island becomes smaller. To understand this difference it is useful to consider the thermodynamic theory of Ostwald ripening (see e. g. chapter 10.4 of [26]). According to that theory, the linear decay in time is characteristic for the “detachment limited” decay while the increased rate with smaller islands indicates the “diffusion limited” decay. Diffusion limited decay occurs when the barrier for the attachment of an atom to a kink site is equal or smaller than the barrier for diffusion. According to Fig. 1 and 2 this is the case here. The experimentally observed curved shape of the decay curve is therefore expected from the potential curves in Fig. 1 and 2. The decay rate for an island of radius $\hat{r}_\mathrm{i}$ (in units of atom diameters) in a vacancy island of radius $\hat{r}_\mathrm{o}$. In units of atom diameters) is [26]

$$\frac{\mathrm{d}N}{\mathrm{d}t} \cong -\frac{2\pi\hat{\beta}}{k_\mathrm{B}T} k_0 \mathrm{e}^{-\Delta E/k_\mathrm{B}T} \mathrm{e}^{-E_b/k_\mathrm{B}T} \frac{1}{\hat{r}_\mathrm{i}(t)\ln(r_\mathrm{o}/r_\mathrm{i}(t))} \tag{1}$$

in which $\hat{\beta}$ is the step line tension per step atom, k_0 and ΔE are prefactor and activation energy for diffusion (Table 1), and E_b is the binding energy of the diffusing unit with reference to the kink site. With k_0, ΔE and E_b taken from our DFT calculations, the initial experimental island radius $\hat{r}_\mathrm{i} = 23$, the vacancy island radius $\hat{r}_\mathrm{o} = 38$ taken from experiment and a step line tension of 0.5eV one obtains $\mathrm{d}N/\mathrm{d}t = -0.8$ atoms/s, which is in excellent agreement with the experimental decay rate (Fig. 3). The same calculation applied to the island size used in the simulation would yield just about the same rate, hence a rate which is a factor of four larger than actually obtained from the simulations. While this is still a reasonable agreement one wonders why the decay is linear in time rather than following the curvature according to eq. 1. The reason is presumably that eq. 1 assumes quasi-equilibrium between the chemical potential of the islands and the local concentrations of adatoms on the terrace. The net flux away from the center island to the vacancy island is then due to the different Gibbs-Thomson chemical potentials of the islands. In kinetic Monte Carlo simulations on small systems equilibrium is not reached. All atoms released from a kink site are captured by a kink site of either the center island or the vacancy island before the next adatom is released. In that case the decay should be always detachment limited, hence linear in time.

In summary, we find that our DFT calculations and Monte Carlo simulations are in qualitative and quantitative agreement with experimental observations on island decay on Au(100) surfaces under potential control in electrolytes.

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