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Equilibrium coverage of halides on metal electrodes

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ABSTRACT

The adsorption of halides on Cu(111) and Pt(111) has been studied using periodic density functional theory calculations. The equilibrium coverage of the halides as a function of the electrode potential was determined using a thermodynamic approach in which the electrochemical environment is not explicitly taken into account. For all considered systems, halide coverages between 1/3 and 3/8 should be stable over a wide potential range. Although some quantitative discrepancies with experiment are obtained, the qualitative trends derived from the calculations are consistent with experimental observations. The reasons for the remaining discrepancies with the experiment are discussed.

1. Introduction

The adsorption of anions on metal electrodes is of particular interest in electrochemistry [1,2]. At the electrochemical interface between the electrode and the electrolyte an electric double layer is formed consisting of an electronic charge on the electrode and a corresponding ionic counter charge in the electrolyte [3,4]. Anions such as halides often adsorb specifically, i.e., they form chemical bonds with the metal surface. These adsorbed anions not only affect the chemical properties of electrodes [5] by either directly participating in reactions at the surface or by modifying the electronic properties of the electrodes or by simply blocking adsorption and reaction sites [1], but in general they also change the work function of the electrode, which is directly related to the electrode potential [6].

As part of a systematic effort to model electrode/electrolyte interfaces from first-principles [7–10], we have recently addressed the work function change induced by the adsorption of halides on Cu(111) [11] and on Pt(111) and Ca(111) [12]. In particular, we focused on the anomalous work function change observed at low coverages for some halide/metal systems [13–18] which could be explained either by a polarization of the adatom [11] or a reduction in the surface overspill electron density [12,19].

Here we extend our previous studies in order to determine the equilibrium coverage of halides on Cu(111) and Pt(111). Although recently there is a growing number of first-principles studies addressing structures and processes at electrochemical metal/liquid interfaces [20–28], there have been only few computational attempts to focus on the role of anions on metal electrodes [17,29,30], and it is certainly fair to say that a systematic approach to study anion adsorption on metal electrodes from first-principles in an electrochemical setup is still missing. In an electrochemical situation, the anion coverage on the electrodes is a function of the electrode potential. Although the concentration of anions in the electrolyte is typically relatively low, their concentration on the electrode can be rather high because of their strong interaction with metal electrodes [10,16–18]. However, the exact coverage is often not known.

The realistic modeling of electrochemical metal/liquid interfaces is hampered by three facts: i) In electrochemistry, structures and properties of the electrode–electrolyte interfaces are governed by the electrode potential, which adds considerable complexity to the theoretical treatment since charged surfaces have to be considered [7]. ii) The theoretical treatment of processes at solid–liquid interfaces includes a proper description of the liquid which requires to determine free energies instead of just total energies. This means that computationally expensive statistical averages have to be performed [7,10]. iii) Electronic structure methods based on density functional theory (DFT) combine numerical efficiency with a satisfactory accuracy. However, there are severe shortcomings of the DFT description of liquids, in particular water, using current functionals [31–33].

These problems can be avoided if the electrochemical environment is not explicitly but only implicitly taken into account. In a very elegant approach [34,35] that is now termed “Computational hydrogen electrode” and that is similar to the ab initio thermodynamics approach used in heterogeneous catalysis [36], the electrochemical environment is just considered as a reservoir the adsorbates come from, but the explicit influence of the electrochemical environment on the adsorption properties is not taken into account. This is of course a severe approximation, but it is computationally very attractive, and it allows to establish trends in electrochemistry and electrocatalysis [37].

Here we also use this approach to determine the equilibrium coverage of halides on Cu(111) and Pt(111) in the spirit of the work by Hansen et al. [38]. We will show that the trends in the electrochemical halide coverage observed experimentally can be well reproduced using this approach. Still, discrepancies remain whose possible reasons will be discussed.

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2. Computational details

Periodic DFT calculations that employ the exchange-correlation functional of Perdew, Burke, and Ernzerhof (PBE) [39] were done using the Vienna ab initio program package (VASP) [40]. Electron–core interactions were accounted for by the projector augmented wave method [41,42]. The electronic one-particle wave functions were expanded in a plane-wave basis set up to an energy cutoff of 500 eV.

The metal substrates were represented by slabs of seven atomic layers, of which the inner three layers were kept fixed in the bulk position during geometry optimizations while the rest of the system was allowed to relax. Halogen atoms were placed symmetrically at both sides of the slab. Most of the calculations were performed in a 4×4 surface unit cell for halide coverages between 1/16 and 1/2. The corresponding energy minimum structures for chlorine on Cu(111) are illustrated in Fig. 1. For the integration over the first Brillouin zone we used a mesh of at least $4 \times 4 \times 1$ special k-points [43] with a Methfessel–Paxton smearing [44] of 0.1 eV. In addition, $\sqrt{3} \times \sqrt{3}$ unit cells were used to study different halide coverage of 1/3. Experimentally, halide adsorbate structures with other geometries than those considered in our computational study have been found (see the discussion below). Still, we are mainly interested in qualitative trends and the characteristic differences between the studied systems. Hence we made no effort to address further geometries.

3. Results and discussion

3.1. Theoretical background

The calculated adsorption energies per halogen atom referred to the corresponding free halogen molecule for the considered systems are shown in Fig. 2. The results are in satisfactory agreement with previous computational studies using similar setups (see, e.g., [45]). As a general trend, it can be seen that the adsorption on Cu(111) is stronger than that on Pt(111) although for iodine adsorption the effect is rather small. The trend among the halides is not identical: on Cu(111) chlorine adsorption is stronger than iodine adsorption, while on Pt(111) it is the other way around.

In order to understand these trends, we determined the adsorption energies of the halogen atoms at a coverage of 1/9 on (111) surfaces of Ag, Cu, Ni, Au, Pd, and Pt, where we have ordered the substrates according to increasing work function (see Table 1). In fact, we find a

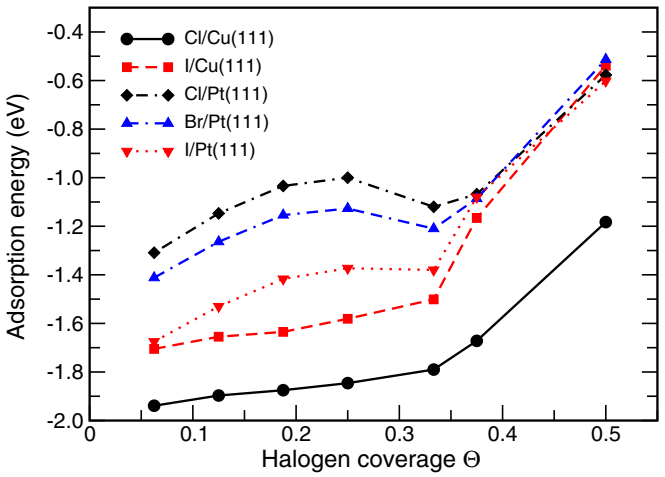

Fig. 2. Adsorption energies of halogen atoms on Cu(111) and Pt(111) with respect to the free halogen molecule as a function of the coverage.

gradual change in the trend in the adsorption energies of Cl, Br, and I. Whereas on Ag and Cu, Cl exhibits the strongest adsorption on Pd and Pt it is I. Thus there is a strong correlation between the work function and the trend in the adsorption energies among the halogen atoms, except for fluorine which exhibits the strongest adsorption of the halogen atoms on all surfaces.

The trend in the adsorption energies, except for fluorine, can then be rationalized as a transition from predominantly ionic bonding to predominantly covalent bonding. Surfaces with low work function such as Ag and Cu easily transfer electronic charge to electronegative adsorbates such as halogen atoms resulting in a more ionic bonding situation. And then the more electronegative (i.e., smaller) halogen atoms exhibit the strongest bonding.

On the other hand, the surfaces with large work function such as Pd and Pt exhibit a smaller charge transfer to electronegative adsorbates so that the bonding becomes mostly covalent in nature, as we already showed [11,12]. And here the more polarizable (i.e., larger) halogen atoms then bind most strongly.

In general, binding to the metal substrates becomes weaker at higher coverage, indicating a repulsive interaction between the adsorbed halogen atoms which becomes particularly evident for coverages $\Theta \geq 1/3$. It

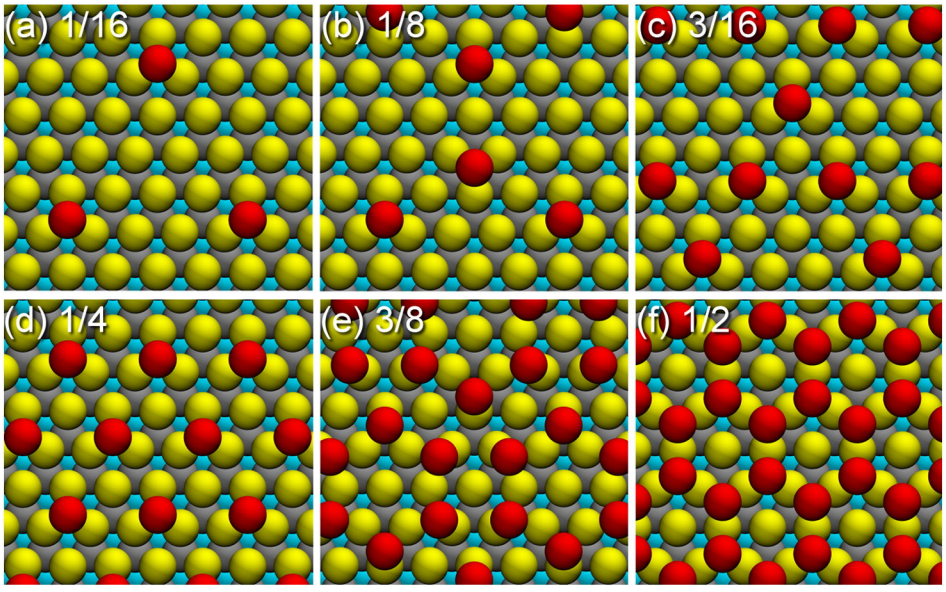

Fig. 1. Relaxed structures of chlorine atoms in a 4×4 geometry on Cu(111) for coverages between 1/16 and 1/2.

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