

Equilibrium coverage of halides on metal electrodes

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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.

Keywords: electrochemistry, density functional theory, halide adsorption, coverage

I. 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 elec-

trode 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.

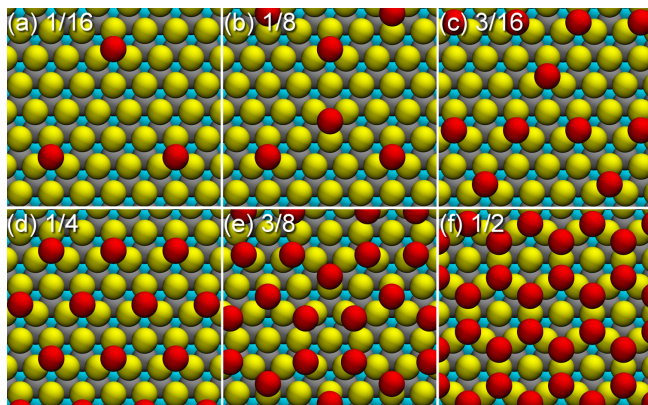


FIG. 1. Relaxed structures of chlorine atoms in a 4×4 geometry on Cu(111) for coverages between $1/16$ and $1/2$.

II. 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.

III. RESULTS AND DISCUSSION

A. 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

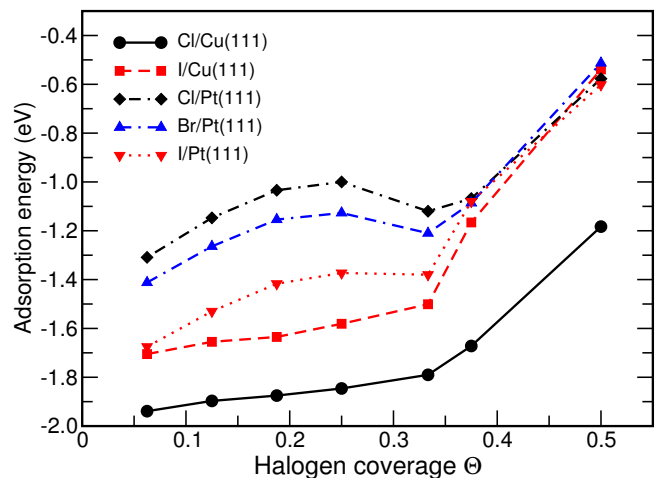


FIG. 2. Adsorption energies of halogen atoms on Cu(111) and Pt(111) with respect to the free halogen molecule as a function of the coverage.

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 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, Pt, where we have ordered the substrates according to increasing work function (see Tab. I). In fact, we find a 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 electronega-

TABLE I. Adsorption energies in eV of halogen atoms with respect to the free halogen molecule on (111) metal surfaces at a coverage of $1/9$. The metal surfaces are ordered according to increasing work function.

E_{ads} (eV)	Ag	Cu	Ni	Au	Pd	Pt
F	-2.61	-2.90	-2.86	-1.84	-2.13	-1.63
Cl	-1.60	-1.86	-2.02	-0.97	-1.66	-1.21
Br	-1.54	-1.75	-1.91	-0.99	-1.70	-1.32
I	-1.40	-1.60	-1.83	-0.99	-1.85	-1.58

tive 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 is also obvious that the halogen coverage $1/3$ corresponding to a $\sqrt{3} \times \sqrt{3}$ structure is rather stable, especially for chlorine and bromine on Pt(111). Note that the $\sqrt{3} \times \sqrt{3}$ structure corresponds to the two-dimensional close-packed structure, but at the same time it is the structure with the largest mutual distances among the adsorbates for a given density. This might explain its stability for adsorbates that repel each other such as halides.

From the adsorption energies shown in Fig. 2 it is, however, not directly clear what the thermodynamically stable structures under specific conditions are. In order to address this issue, we will first briefly recall the theoretical background for the determination of an adsorbate coverage in thermal equilibrium. It is important to note that in equilibrium, every species is characterized by its chemical potential which is constant throughout the whole system. At gas/solid interfaces – as they occur in heterogeneous catalysis – the Gibbs free energy of adsorption $\Delta\gamma$ for N_{ads} adsorbates bound to a surface area A_s at a given temperature T and pressure p can be expressed [36] as

$$\Delta\gamma(T, p) = \gamma(T, p, N_{\text{ads}}) - \gamma_{\text{clean}}(T, p, 0) \quad (1)$$

$$= \frac{1}{A_s} \Delta G^{\text{ads}}(T, p) \quad (2)$$

$$= \frac{N_{\text{ads}}}{A_s} (E_{\text{ads}} - \mu_{\text{ads}}(T, p)) . \quad (3)$$

Here, $\Delta G^{\text{ads}}(T, p)$ is the difference in free energy and $\mu_{\text{ads}}(T, p)$ is the chemical potential of the adsorbate. In the last equation (3) above, E_{ads} is the total adsorption energy per particle, and any change in entropy and zero-point energies upon adsorption is neglected, as often done in theoretical studies addressing systems in heterogeneous catalysis and surface science [36].

In the adsorption at electrochemical interfaces, the reference state corresponds to species in solution in the presence of an electrode potential U . This means that the chemical potential μ has to be replaced by the electrochemical potential

$$\tilde{\mu} = \mu + neU, \quad (4)$$

where n is the charge of the particle. Still the problem remains that the electrochemical potential includes

all solvation effects of the species. The determination of solvation energies requires computationally demanding thermal integration schemes [46]. These efforts can be avoided using the concept of the computational hydrogen electrode. It is based on the fact that at standard conditions ($\text{pH} = 0$, $p = 1$ bar, $T = 298$ K) $U = 0$ is defined as the electrode potential at which there is an equilibrium between a proton and an electron in aqueous solution $\text{H}^+(\text{aq}) + e^-$ and hydrogen in the gas phase, $\frac{1}{2}\text{H}_2(\text{g})$. Furthermore, it is well known how the electrochemical potential of the proton and the electron change if the proton concentration and the electrode potential is varied [47], namely according to

$$\tilde{\mu}(\text{H}^+(\text{aq})) + \tilde{\mu}(e^-) = \frac{1}{2}\mu(\text{H}_2(\text{g})) - eU_{\text{SHE}} - k_{\text{B}}T \ln(10)\text{pH}, \quad (5)$$

where U_{SHE} is the electrode potential with respect to the standard hydrogen electrode (SHE). The success of the computational hydrogen electrode is based on the fact that it allows to derive adsorption energies with respect to solvated species without the need to determine any solvation energies.

This concept does not only work for hydrogen, it works also for any redox couple $\frac{1}{2}\text{A}_2 + e^- \rightleftharpoons \text{A}^-$, as applied by Hansen *et al.* to describe the electrochemical chlorine evolution at rutile oxide (110) surfaces [38]. Here we follow the same approach (note that there are typos in Ref. [38] in the corresponding equations), i.e., we derive the electrochemical potential for a halide A, where A stands for Cl, Br or I, as

$$\tilde{\mu}(\text{A}^-(\text{aq})) - \tilde{\mu}(e^-) = \frac{1}{2}\mu(\text{A}_2(\text{g})) + e(U_{\text{SHE}} - U^0) + k_{\text{B}}T \ln a_{\text{A}^-}, \quad (6)$$

where U^0 is the reduction potential of the corresponding halide and a_{A^-} its activity. The reduction potentials for the halides considered in this study are collected in Tab. II.

The change of zero-point energies upon adsorption of the halogen atoms can safely be neglected [48] mainly because of their relatively large mass. For example, in the adsorption of chlorine on rutile oxide (110) surfaces they have been estimated to be in the order of 0.02 eV [38]. Furthermore, we also neglect the entropy change upon adsorption. In the following, we will also assume standard conditions, i.e., we assume that the activity of the halides a_{A^-} is unity. Thus we arrive at the following expression for the free energy of adsorption as a function

TABLE II. Reduction potentials of the halides considered in this work.

Redox couple	Reduction potential U^0 (V)
$\frac{1}{2}\text{Cl}_2 + e^- \rightleftharpoons \text{Cl}^-$	1.36
$\frac{1}{2}\text{Br}_2 + e^- \rightleftharpoons \text{Br}^-$	1.09
$\frac{1}{2}\text{I}_2 + e^- \rightleftharpoons \text{I}^-$	0.54

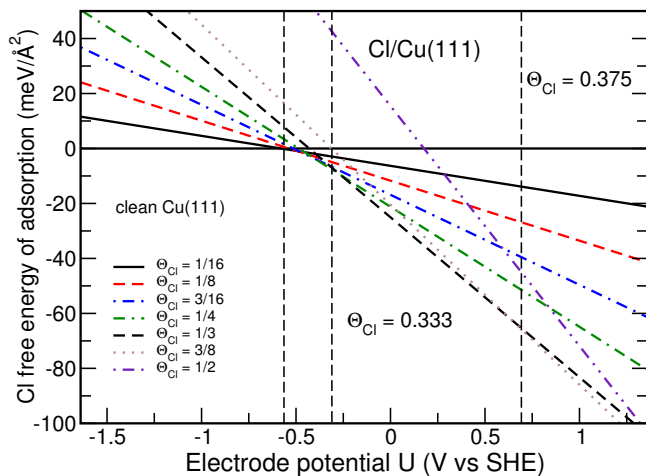


FIG. 3. Calculated electrochemical equilibrium coverage of chlorine on Cu(111) at standard condition as a function of the electrode potential vs. SHE.

of the electrode potential,

$$\Delta\gamma(U_{\text{SHE}}) = \frac{N_{\text{ads}}}{A_s} (E_{\text{ads}} - e(U_{\text{SHE}} - U^0)) . \quad (7)$$

For other concentrations of the halides in the electrolyte, the electrode potential needs to be shifted by $k_B T \ln a_A$ which corresponds, e.g., to about 60 meV if the activity is changed by one order of magnitude at room temperature.

It should be emphasized that within our approach, the adsorption energy E_{ads} appearing in Eq. 7 is calculated without taking the electrochemical environment into account. Furthermore, the varying excess charge at the metal electrodes as a function of the electrode potential is also not considered. These are certainly severe approximations. Comparing our results with experimental findings is a first step to assess the validity of this approach.

B. Halides on Cu(111)

The first system we discuss is the adsorption of chlorine on Cu(111) which is a rather well-studied system in electrochemistry [1, 49–52], among others motivated by the fact that chloride adlayers on copper electrodes are of major importance in corrosion and electroplating. Although there was some debate about the equilibrium structure of chloride on Cu(111), more recent studies indicate that a simple $\sqrt{3} \times \sqrt{3}$ structure with a coverage of 1/3 should result in an electrochemical environment [49, 51]. In addition, a compressed chloride adlayer has been suggested [50, 52]. It should be noted that on Cu(100) even nominal coverages of 1/2 have been observed [1, 29].

Our prediction concerning the equilibrium structure of chlorine on Cu(111) as a function of the electrode poten-

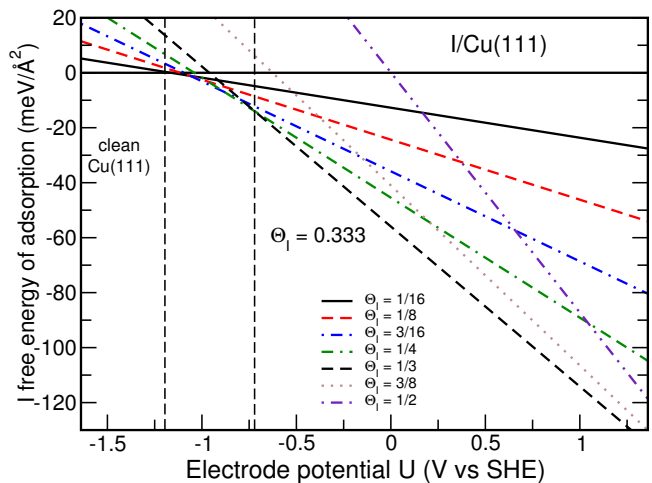


FIG. 4. Calculated electrochemical equilibrium coverage of iodine on Cu(111) at standard condition as a function of the electrode potential vs. SHE.

tial at standard conditions are shown in Fig. 3. Note that these diagrams can be read as a kind of phase diagram. The structure with the lowest free energy of adsorption is supposed to be the thermodynamically stable structure. In Fig. 3 and the following figures we show the free energy curves in a potential range of about 3 eV. This is larger than the stability range of some of the considered systems. Still we have chosen such a broad range in order to make the diagrams clearly arranged.

We find that at potentials below -0.6 V, the clean Cu(111) electrode is stable. Between -0.6 V and -0.3 V, structures with increasing coverage become stable before at -0.3 V a large potential window opens in which the $\sqrt{3} \times \sqrt{3}$ structure is assumed to be realized in thermodynamical equilibrium. The onset of the formation of the chloride adlayer at about -0.3 V is consistent with the peaks assigned to the adsorption and desorption of Cl in cyclic voltammograms [49–51].

Hence our calculations confirm the prominent role the $\sqrt{3} \times \sqrt{3}$ structure plays for the adsorption of chlorine on Cu(111) under electrochemical conditions. The compressed chlorine adlayers which have been found on Cu(111) [50, 52] cannot be addressed by our periodic setup as they have been identified to be an incommensurate adlayer with a rotated hexagonal structure [52]. Still, the fact that we find a chlorine adlayer structure corresponding to a coverage of $\Theta_{\text{Cl}} = 3/8$ which is almost as stable as the $\Theta_{\text{Cl}} = 1/3$ structure indicates that compressed chlorine adlayer structures with coverages slightly above 1/3 should indeed be possible.

Next, we address the equilibrium structures of iodine on Cu(111). Experimentally, basically only the $\sqrt{3} \times \sqrt{3}$ structure was observed [50]. Although initially no compression of the iodine adlayer as a function of the electrode potential was observed [50], later studies found uniaxially incommensurate iodide adlayers caused by a

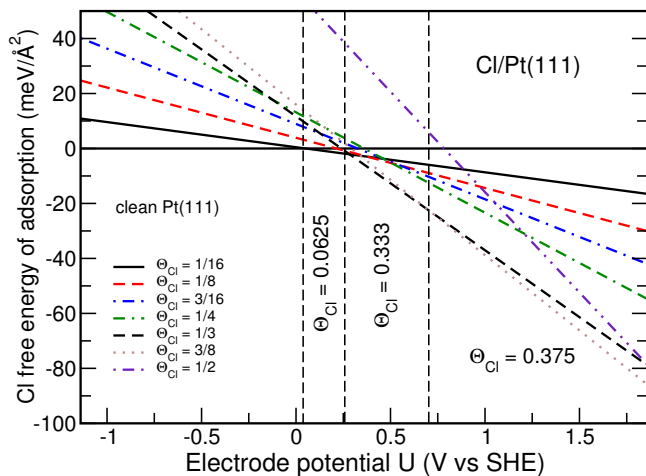


FIG. 5. Calculated electrochemical equilibrium coverage of chlorine on Pt(111) at standard condition as a function of the electrode potential vs. SHE.

unidirectional compression of the $\sqrt{3} \times \sqrt{3}$ -I at vacuum at higher iodine coverages [53] or in an electrochemical environment at more positive potentials close to the onset of the copper dissolution reaction [54].

The calculated free energy of adsorption of iodine on Cu(111) as a function of the electrode potential is plotted in Fig. 4. Iodine adsorption on Cu(111) occurs at lower potentials than chlorine adsorption which is in qualitative agreement with the experiment [51, 54] although iodine adsorption on Cu(111) is weaker than chlorine adsorption, as Fig. 2 demonstrates. This lower onset potential is caused by the fact that the reduction potential of iodine is much lower than the one of chlorine (see Tab. II).

We find a potential region between -1.2 V and -0.7 V in which a series of structures with increasing coverage becomes stable. At potentials above -0.7 V, only the $(\sqrt{3} \times \sqrt{3})$ structure is found. Again, the uniaxially incommensurate compressed iodide adlayer could not be addressed by the periodic calculations since the corresponding superstructures are too large. For I/Cu(111), the $\Theta = 3/8$ is more unfavorable compared to the $\Theta = 1/3$ than in the case of Cl/Cu(111). This is consistent with fact that Inukai *et al.* did not find any compression of the iodine adlayer in the potential window between -0.5 V and -0.7 V vs. SCE [50].

C. Halides on Pt(111)

Turning to the Pt(111) electrode, we start with the system Cl/Pt(111). Using *in situ* surface x-ray scattering, Lucas *et al.* were not able to detect any ordered chlorine adlayer over the entire potential range where chloride is present on the Pt(111) electrode [55]. They estimated the chloride coverage to be between 0.4 and 0.6. To the best of our knowledge, there is no study revealing an atom-

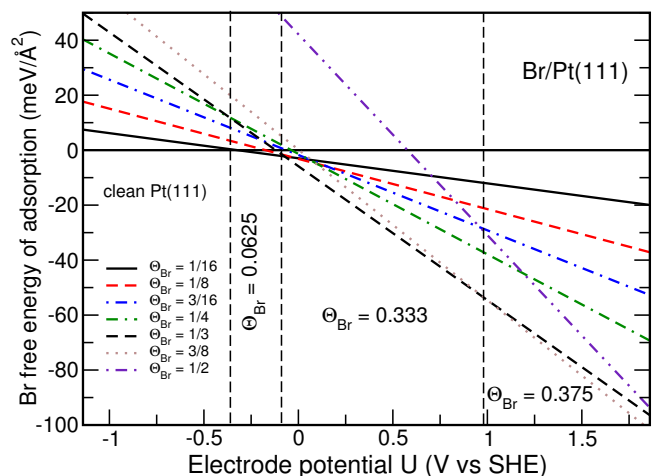


FIG. 6. Calculated electrochemical equilibrium coverage of bromine on Pt(111) at standard condition as a function of the electrode potential vs. SHE.

istic structure of chlorine on Pt(111) in an electrochemical environment. In a chronocoulometric study [56], the structure of Cl/Pt(111) was not addressed, however, it was found that the adsorbed species is basically a neutral chlorine atom which agrees nicely with our computational findings [12].

We find (see Fig. 5) that at standard conditions a chlorine adlayer on Pt(111) should start to form at potentials close to 0 V. This is a significantly higher onset-potential than on Cu(111) because of the weaker binding of chlorine to Pt(111) (see Fig. 2). Up to about 0.25 V, a chlorine layer with a coverage of 1/16 should be stable, followed by the $\sqrt{3} \times \sqrt{3}$ structure. This $\Theta = 1/3$ structure, however, is only stable up to 0.7 V where $\Theta = 3/8$ becomes more favorable. Furthermore, the layers corresponding to $\Theta = 1/3$ and $\Theta = 3/8$ are rather close in energy. This might yield an explanation why no specific ordered structure could be identified in the experiment [55].

For bromine on Pt(111), *in situ* STM experiments yielded asymmetric and hexagonal (3×3) structures at a coverage of $\Theta = 4/9$ [57]. Using X-ray scattering experiments, Lucas *et al.* [55] observed a series of high-order commensurate structures as a function of electrode potential which are poorly ordered unless the size of the unit cell is small. These unit cells corresponded to (3×3) and (7×7) structures with coverages of $\Theta = 4/9$ and $\Theta = 25/49$, respectively. Based on rotating disk experiments, Gasteiger *et al.* [58] found that in 0.1 M HClO₄ with 10^{-4} M Br⁻ bromide adsorption starts at about 0.1 V and reaches a coverage of about $\Theta = 0.42$ at 0.75 V.

As shown in Fig. 6, according to our calculations bromine starts to adsorb on Pt(111) at standard conditions at about -0.35 V with a $\Theta = 1/16$ structure. This onset occurs at lower potentials than chlorine adsorption on Pt(111) because both the bromine bonding to

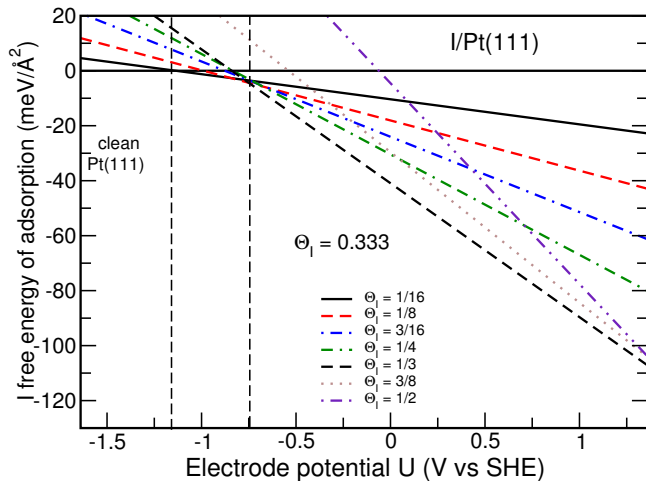


FIG. 7. Calculated electrochemical equilibrium coverage of iodine on Pt(111) at standard condition as a function of the electrode potential vs. SHE.

Pt(111) is stronger than the chlorine bonding, and the reduction potential of bromine is lower than the one of chlorine. In a wide potential range from -0.1 V and 1.0 V, the $(\sqrt{3} \times \sqrt{3})$ structure with $\Theta = 1/3$ is stable, followed above 1.0 V by the $\Theta = 3/8$ structure. Similar to Cl/Pt(111), the layers corresponding to $\Theta = 1/3$ and $\Theta = 3/8$ are rather close in energy.

In our calculations, we did not consider (3×3) and (7×7) structures, hence we cannot compare our results directly with experiment [55]. Still, our results are consistent with the fact that over a wide range of potentials, bromine coverages of $\Theta \geq 0.4$ have been found. Note that the $k_B T \ln a_{\text{Br}^-}$ term in eq. 6 leads to a shift of the free energy curves by about 60 mV to higher potentials if the activity is decreased by one order of magnitude. Furthermore, increasing the pH-value of the electrolyte by one leads to the same shift. Considering such a shift, the observed potential range for bromide adsorption on Pt(111) [58] is compatible with our calculated order of stability.

In ultrahigh vacuum (UHV), iodine dosing of a Pt(111) leads to two ordered structures, $(\sqrt{3} \times \sqrt{3})$ with a coverage of $\Theta = 1/3$ and $(\sqrt{7} \times \sqrt{7})R19.1^\circ$ with $\Theta = 3/7$ [59]. In temperature-programmed desorption (TPD) experiments, Jo and White [15] observed a shift of the desorption peaks to lower temperatures with increasing coverage which is consistent with the lower iodine binding energies for higher coverages shown in Fig. 2. In addition, they found a non-monotonic decrease of the I/Pt(111) work function as a function of the iodine coverage which is well reproduced by our calculations [12]. Early *in situ* STM experiments confirmed the existence of the $(\sqrt{3} \times \sqrt{3})$ structure also in an electrochemical environment [60]. Later X-ray scattering [55] and *in situ* STM experiments [61] found the coexistence of a hexagonal (3×3) structure with $\Theta = 4/9$ and the $(\sqrt{7} \times \sqrt{7})R19.1^\circ$

structure under potential control.

Again, we have considered neither the (3×3) nor the $(\sqrt{7} \times \sqrt{7})R19.1^\circ$ structure. As Fig. 7 shows, our calculations yield that iodine adsorption starts at -1.2 V, and above -0.75 V only the $(\sqrt{3} \times \sqrt{3})$ is stable. As our calculations are done at the solid-vacuum interface, it is no surprise that the UHV structure of I/Pt(111) has been reproduced.

The onset potential of iodine adsorption on Pt(111) is very close to the one on Cu(111) because of the similar adsorption energies (see Fig. 2). Interestingly enough, whereas iodine adsorption on Pt(111) is stronger than chlorine adsorption on Pt(111), it is the other way around on Cu(111), which means that there is no general trend of the adsorption energies among the halides for metal electrodes.

D. Discussion

In the previous sections, we have compared experimental findings with respect to the stability of halide structures on Cu(111) and Pt(111) at electrochemical conditions with the predictions of a very simple thermodynamical model that does not explicitly take into account the electrochemical environment. The calculated stability range of the halide structures and together with their corresponding coverage are in qualitative or even in semi-quantitative agreement. However, some characteristic quantitative difference between experiment and the simple thermodynamic model remain. This is partially due to the fact that we did not consider all structures observed in the experiment. Still, there are three main reasons that could be responsible for the discrepancies.

First of all, the change of the adsorption energy for varying surface excess charge or varying electric fields has not been taken into account. According to a DFT study, electric field effects should only play a minor role in the oxidation reaction on Pt(111) [62], however, it is not clear whether these findings can be transferred to halide adsorption.

Second, the aqueous environment was not explicitly considered. Now water is relatively weakly interacting with metal electrodes [7, 63, 64] so that chemisorption energies are only weakly influenced by the presence of water [65, 66]. Therefore we do not expect that water layers change the adsorption energies of the halides significantly. However, reorientation of the water molecules due to the presence of the halides might still affect the work function of the electrodes and thus the corresponding electrode potential.

Third, the presence of additional adsorbates is not taken into account. This is particularly important for Pt(111) where at low potentials hydrogen adsorption [67, 68] and at higher potentials OH adsorption take place. There might be some competition for the adsorption sites. Furthermore, co-adsorbates influence the adsorption energy either through direct adsorbate-

adsorbate interactions or indirectly through modifying the electronic properties of the substrate [69, 70]. Both effects might affect the stability of the halide adsorption phases.

Last but not least, it should be mentioned that errors might of course also be introduced through the approximate nature of the exchange-correlation functional used in the DFT calculations. A quantitative assessment of the reliability of the functional, however, can only be achieved once the electrochemical interface is realistically modeled. Such a realistic modeling of the structure of electrochemical interfaces is not only interesting in its own right, it is also crucial for a reliable description of electrocatalytic processes as they occur, e.g., in fuel cells. Therefore we are in the process of studying the importance of all the effects discussed above in our ongoing work.

IV. CONCLUSIONS

Using a very simple thermodynamical model corresponding to the computational hydrogen electrode [34, 35], we have estimated the stability of halide structures on Cu(111) and Pt(111). According to our calculations,

for all considered systems halide coverages between 1/3 and 3/8 should be stable in a wide potential range. Although in this model the electrochemical environment at the interface is not explicitly taken into account, the theoretical results are consistent with experimental observations. Thus this model offers a computationally convenient way to estimate anion coverages at electrochemical interfaces under potential control. Still further work is needed in order to assess the importance of the effects neglected in the simple thermodynamical model.

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