Modeling of the Coadsorption of Chloride and Hydrogen Ions on Copper Electrode Surface

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For manufacturing copper interconnects by the damascence technique, electrochemical deposition of copper on patterned substrates requires several additives to achieve compact filling of trenches and vias, where chloride ions play a crucial role. In the highly acidic electrolyte, adsorption of chloride ions on copper is expected to compete with the adsorption of hydrogen, depending on the copper electrode potential. We propose a general phenomenological model of the coadsorption of two ion species which is supported by DFT calculations and show how the adsorption of one species can be described by the common Langmuir model with rescaled parameters depending on the concentration of the second species. Regarding the Cl⁻-H⁺-system, corresponding model parameters are estimated by fitting radio tracer measurements of the chloride adsorption on copper reported in the literature. The data suggest that in a highly acidic solution (pH ≈ 0) the saturation surface density of chloride depends strongly on the electrode potential.

In this case, the equilibrium surface coverage of chloride can approximately be expressed in the form of the standard Langmuir isotherm for a single species, where the kinetic parameters depend on the concentration of hydrogen ions. We think that previously reported models of copper deposition, which include chloride adsorption, could easily be amended to take into account the chloride-hydrogen-coadsorption effect by properly adjusting the corresponding parameters.

Coadsorption Model

Coadsorption kinetics.—In the following, we present a Langmuir-like model for the coadsorption of two species on a common surface, where additional interaction parameters are introduced, by which the mutual influence of the two species on their adsorption is taken into account in a phenomenological manner. The kinetics for the coadsorption of two species, A and B, is modeled by the following coupled equations for the temporal evolution of the surface densities

\[
\dot{\Gamma}_A = k_a^A \Gamma_A^0 \theta_A^{free} - k_d^A \Gamma_A,
\]

\[
\dot{\Gamma}_B = k_a^B \Gamma_B \theta_B^{free} - k_d^B \Gamma_B.
\]

where \(\Gamma \equiv d\Gamma_i/dt\), \(\Gamma_i\) with \(i = [A, B]\) is the surface density of the \(i\)-th ion species, \(\Gamma_i^0\) is the maximal surface density in the absence of the other species, \(c_i\) is the ion density in the solution, and \(k_a^i\) and \(k_d^i\) are the adsorption and desorption coefficients, respectively. Further, \(\theta_i^{free}\) is the free surface for the adsorption of the corresponding ion species normalized by the total substrate surface, which is expressed as

\[
\theta_A^{free} = 1 - \Gamma_A / \Gamma_A^0 - \alpha \Gamma_B / \Gamma_B^0,
\]

\[
\theta_B^{free} = 1 - \Gamma_B / \Gamma_B^0 - \beta \Gamma_A / \Gamma_A^0,
\]

where the last term on the rhs of the equations represents the hindering of the adsorption of one species by the adsorbed molecules of the other species. The corresponding factors \(\alpha\) and \(\beta\) determine the degree of the hindering. The values of these factors are related to the special kind of the interaction of the two species on the surface. In the following, we consider different cases of this interaction.

(A) Within a simple mechanistic view, the adsorbed species can be considered as rigid bodies covering a species-dependent area \(a_i\) on the surface. As the only interaction between the adsorbed molecules, area exclusion between the molecules leads to the following equation

\[
\theta_A^{free} = \frac{A - N_A a_A - N_B a_B}{A} = 1 - \frac{\Gamma_A / \Gamma_A^0 - \Gamma_B / \Gamma_B^0}{1 / \Gamma_A^0}
\]

where \(N_i\) are the total numbers of the adsorbed species on the total surface \(A\). In the second equation, the relations \(\Gamma_i = N_i / A\) and \(a_1 = 1 / \Gamma_1^0\) were used. The same expression results for species B, i.e., \(\theta_B^{free} = \theta_A^{free}\). Comparison with Eqs. 3 and 4 shows that it corresponds to the limiting case \(\alpha = \beta = 1\).

In general, the interaction between the molecules is more complex. Within an atomistic view, different species may have different

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preferred adsorption sites on the substrate surface (for example fcc or hcp hollow sites, bridge sites, or on top of substrate atoms).

(B) As a more complex example, one may imagine that the surface area $N_{SB}$, covered by adsorbed species B, is not completely covered for adsorption of species A. Only within a certain surface part $\alpha N_{SA}$ ($\alpha < 1$) species A cannot be adsorbed. Analogously, only the surface part $\beta N_{SB}$ ($\beta < 1$) is considered to be unavailable for adsorption of species B. Then, the normalized free surfaces for the two species are given by
\[
\theta_A^{free} = \frac{(A - N_{SA}) - \alpha N_{SB}B}{A} \tag{6}
\]
\[
\theta_B^{free} = \frac{(A - N_{SA}) - \beta N_{SB}A}{A} \tag{7}
\]
from which Eqs. 3 and 4 follow.

(C) A further example, which demonstrates the meaning of the coefficients $\alpha$ and $\beta$, is a system where each species has its own set of adsorption sites ($\Gamma_A^{0}$ and $\Gamma_B^{0}$). These sites could be disjunct, e.g. species A on hollow sites and species B on top sites. We consider here a more general case where the two species share some common sites as well. Assuming species B to be evenly distributed over common and non-common sites, the surface density of free sites for each species reads
\[
\theta_A^{free} = \Gamma_A^{0} - \Gamma_A - \frac{\Gamma_A^{0} + \beta \Gamma_B^{0}}{1 + \alpha \Gamma_B^{0} / \beta \Gamma_B^{0}} \tag{8}
\]
\[
\theta_B^{free} = \Gamma_B^{0} - \Gamma_B - \frac{\Gamma_A^{0} + \alpha \Gamma_B^{0}}{1 + \beta \Gamma_B^{0} / \alpha \Gamma_B^{0}} \tag{9}
\]
where in the second equations the quantities $\alpha = \Gamma_A^{0} / \Gamma_B^{0}$ and $\beta = \Gamma_B^{0} / \Gamma_B^{0}$ have been introduced. Using the relations $\theta_i^{free} = \Gamma_i^{free} / \Gamma_i^{0}$, we obtain again Eqs. 3 and 4.

(D) For certain systems, replacement processes of an adsorbed species by the other species can be relevant. For instance, adsorbed chloride ions on a copper surface could be replaced by hydrogen ions in solution (compare the results of DFT calculations below). For a system of species A and B, where species B in solution are able to adsorb on a copper surface, the replacement processes can be taken into account by the following kinetic equations
\[
\dot{\Gamma}_A = k_A c_A \Gamma_A^{0} \theta_A^{free} - k_A^c B \Gamma_A - k_A^B \Gamma_A \tag{10}
\]
\[
\dot{\Gamma}_B = k_B^c A \Gamma_B^{0} \theta_B^{free} + k_B A \Gamma_B - k_B^B \Gamma_B \tag{11}
\]
where $k_A$ is the kinetic coefficient for the replacement of species A by species B. With the simple approximation 5, i.e. $\theta_i^{free} = 1 - \Gamma_i^{0} / \Gamma_i^{0}$, Eqs. 10 and 11 can be rewritten in a form similar to Eqs. 1 and 2
\[
\dot{\Gamma}_A = k_A^c c_A \Gamma_A^{0} \theta_A^{free} - (k_A^c + k_B^c B) \Gamma_A \tag{12}
\]
\[
\dot{\Gamma}_B = k_B^c A \Gamma_B^{0} (\theta_B^{free} + k_B A \Gamma_B) - k_B^B \Gamma_B \tag{13}
\]
By comparing with Eqs. 1 to 4, one finds that $\theta_A^{free} = \theta_B^{free}$ and $\theta_B^{free} = \theta_A^{free} + k_B \Gamma_A / (k_B^c \Gamma_B^{0})$. Thus, in the case of an additional replacement mechanism, the kinetic equations can be reformulated in a manner as in Eqs. 3 and 4 where the parameters $\alpha$ and $\beta$ take the values $\alpha = 1$ and $\beta = 1 - k_B^c \Gamma_B^{0} / (k_B^c \Gamma_B^{0})$.

Generally, the interactions between the adsorbed and with the substrate are very complex. The different scenarios listed above, represent limiting cases and are not mutually exclusive. One example corresponding to case (A) would be the adsorption of inert gases. Strongly different repelling interactions between adsorbed species could lead to a situation considered in case (B). For case (C), it is important that the two species occupy different surface sites of the substrate as for example top and hollow sites. As an example of the replacement scenario (D), we consider below the chlorine-hydrogen-system.

Equilibrium surface densities.—The equilibrium surface densities of the two species in the coadsorbed state are given by the stationary limit $\Gamma_A^0 = \Gamma_B^0 = 0$ of Eqs. 1 and 2. By inserting into these equations formulas 3 and 4 for the normalized free surfaces $\theta_i^{free}$ and $\theta_j^{free}$, one finds the equilibrium densities
\[
\Gamma_A^0 = \kappa_A c_A \frac{1 + (1 - \alpha) k_B c_B}{1 + k_A c_A + k_B c_B + (1 - \alpha) k_A c_A k_B c_B} \tag{14}
\]
\[
\Gamma_B^0 = \kappa_B c_B \frac{1 + (1 - \beta) k_A c_A}{1 + k_A c_A + k_B c_B + (1 - \beta) k_A c_A k_B c_B} \tag{15}
\]
where the abbreviations $\kappa_i = k_i^c / k_i^B$ have been introduced. If one of the two species is absent, these formulas reduce to the common Langmuir isotherm for a single species. For example for $c_B = 0$, one obtains $\Gamma_A^0 = \Gamma_A^0 / (1 + 1 / (k_B c_A))$.

An interesting question is the value of the surface densities in the limit of very high bulk concentration of one species, e.g. for $c_A \to \infty$. In this limiting case, one finds for the saturation surface densities
\[
\Gamma_A^S = \Gamma_A^0 = \frac{1 + (1 - \alpha) k_B c_B}{1 + (1 - \alpha) k_B c_B} \Gamma_A^0 \tag{16}
\]
\[
\Gamma_B^S = \frac{\Gamma_B^0}{1 + (1 - \beta) k_A c_A} \tag{17}
\]
Thus, we get the remarkable prediction that the saturation surface density $\Gamma_A^B$ of species A is generally less than $\Gamma_A^0$ and depends on the concentration of species B in the solution. Species A reach full coverage $\Gamma_A^S = \Gamma_A^0$ only if coefficient $\beta = 1$, or for the trivial case $c_B = 0$.

In the following, we show how the derived expressions for the coadsorption of two species can be reformulated as the common Langmuir model for the adsorption of one species only. The kinetic equation for the adsorption of a single species, say A, reads
\[
\frac{d\Gamma_A}{dt} = \dot{\Gamma}_A^0 c_A \frac{\Gamma_A^S - \Gamma_A}{\Gamma_A^S - \Gamma_A^0} \tag{18}
\]
We have labeled the quantities in the last equation with a tilde to distinguish them from those introduced above. The corresponding equilibrium surface density can be expressed in the following way
\[
\frac{1}{\Gamma_A^S} = \frac{1}{\Gamma_A} + \frac{1}{\Gamma_A^0} \frac{1}{\kappa_A c_A} \tag{19}
\]
where $\kappa_A = \dot{\kappa}_A^c / \dot{\kappa}_A^c$. Our result for $\Gamma_A^S$ in the case of the coadsorption of two species, Eq. 14, can be rewritten in a form similar to Eq. 19. By using the expression 16 for the saturation density $\Gamma_A^S$, one finds
\[
\frac{1}{\Gamma_A^S} = \frac{1}{\Gamma_A} + \frac{1}{\Gamma_A^0} \frac{1 + k_B c_B}{1 + (1 - \alpha) k_B c_B + (1 - \beta) k_A c_A} \tag{20}
\]
Comparison of Equations 19 and 20 reveals how the parameters in the common Langmuir model for the description of the adsorption isotherm of only one species are affected by the presence of a second species. The corresponding parameters are rescaled in the following way
\[
\kappa_A = \frac{1 + (1 - \alpha) k_B c_B}{1 + (1 - \alpha) k_B c_B + (1 - \beta) k_A c_A} \tag{21}
\]
\[
\dot{\kappa}_A = \frac{1 + (1 - \alpha) k_B c_B}{1 + k_B c_B} \kappa_A \tag{22}
\]
Equations 21 and 22 show how the concentration $c_B$ of species B in the bulk solution influences the adsorption of species A.

Potential dependence of kinetic coefficients.—The temperature dependence of the adsorption and desorption rate constants are commonly written as an Arrhenius equation
\[
k = k_0 e^{-Ea/k_B T} \tag{23}
\]
where $k_0$ is a prefactor and $E_a$ the activation energy. The adsorption or desorption of charged species (e.g. H$^+$ and Cl$^-$) represent a charge transfer process. Thus, the activation energy will have a contribution due to the bias potential $E$

$$E_a = E_{a,0} + e\Delta E$$

[24]

where $e\Delta \mu = e(z^+ - z)$ is the charge transfer between the barrier state with charge $z^+$ and the corresponding adsorption or desorption state with charge $z^+$ or $z^-$, respectively. This leads to the following potential dependence of the adsorption and desorption rate constants of species $i$

$$k_i^a = k_i^d \exp(-E_{a,0} + e\Delta E_i / k_B T)$$

[25]

$$k_i^d = k_i^a \exp(-E_{a,0} + e\Delta E_i / k_B T)$$

[26]

Using these expressions, we finally find the potential dependence of the characteristic variables $\kappa_i$ in Equations 14 and 15 for the equilibrium coverages $\theta_{\text{eq}}$.

$$\kappa_i = K_i \exp(-B_i E)$$

[27]

where $K_i = (k_{i,a}^d / k_{i,d}^d) \exp((E_{i,a}^d - E_{i,d}^d)/k_B T)$ and $B_i = e(z_i^+ - z_i^-)/k_B T$ have been introduced. Here $e(z_i^+ - z_i^-)$ is the charge transfer due to ion adsorption. A similar exponential dependence of the adsorption and desorption rate constants on the bias potential has been proposed in Refs. 9–11,18–20. In the following, we will apply the proposed model equations for the description of the coadsorption of two ion species in the presence of a bias potential to the Cl$^-$-H$^+$-system.

**Cl-H-Coadsorption on Copper**

**DFT calculations.**—The adsorption of halides on different metal surfaces has been extensively analyzed in the literature within the framework of the spin-polarized density functional theory (DFT). These works concern mainly the adsorption of one species in vacuum (e.g. adsorption on Cu(111)). Only a few works consider the coadsorption of hydrogen and halides. Coadsorption of hydrogen and chloride ions on Pt(111) has been analyzed for example in Ref. 25. To our knowledge, coadsorption of hydrogen and chlorine on copper has not yet studied by DFT. In order to gain insight into the tendencies of the adsorption for this system, we have performed spin-polarized DFT calculations of the Cl-H-coadsorption on the Cu(111) surface. The calculations were done by means of the Vienna ab initio simulation package (VASP), using the PBE generalized gradient approximation (GGA) for the exchange-correlation functional and the PAW method. The wave functions were expanded in plane waves up to a kinetic energy cutoff of 400 eV. The size of the super cell was 3 × 3 × 3 or 6 × 6 depending on the chlorine coverage. The Brillouin zone was sampled by 4 × 4 × 1 k-points using the Monkhorst-Pack scheme for small (large) super cell size. Periodic boundary conditions were applied for all calculations with a gap between the surfaces of 25 Å. Dispersion corrections were included by the standard D2 Grimme parametrization.

As an important issue of the coadsorption, we analyzed whether the replacement of adsorbed chlorine atoms by hydrogen atoms is energetically favorable. To this end, the energy difference between the two states in Figs. 1a and 1b, where one Cl atom is replaced by H, was calculated. The initial Cl coverage was $\theta_{\text{CI}} = 2/9$. Here, the coverage is defined as the number of adsorbed species divided by the number of copper atoms in the topmost (111) surface layer. For the considered atom configurations, we found that the state, where hydrogen replaced chlorine, is energetically unfavorable by 0.6 eV. To be closer to the real electrochemical system, we repeated the calculations for the same set up with initial coverage $\theta_{\text{CI}} = 2/9$, but with explicit consideration of the presence of water molecules. In this case, the replacement of chlorine by hydrogen was found to be energetically favorable with an energy gain of 0.9 eV. In order to quantify the stability of coadsorbed states on Cu(111), we calculated a mean adsorption energy for different surface coverages of chlorine and hydrogen. The corresponding adsorption energy was defined by

$$E_{\text{ads}} = E_{\text{CI}/\text{H/Slab}} - E_{\text{Slab}} - N_{\text{Cl}}/z_{\text{Cl}} E_{\text{HCl}} - N_{\text{H}}/z_{\text{H}} E_{\text{H}_2}$$

[28]

where $E_{\text{CI}/\text{H/Slab}}$ is the total energy of the whole system and $E_{\text{Slab}}$ is the total energy of the copper slab without adsorbate. $E_{\text{H}_2}$ and $E_{\text{HCl}}$ are the energies of the isolated dimers, and $N_{\text{H}}$ and $N_{\text{Cl}}$ are the numbers of adsorbed atoms on the surface. Fig. 2 shows examples of the most stable configurations of coadsorbed states for different coverages with $\theta_{\text{Cl}} = 2/9$. The preferred adsorption sites of both chlorine and hydrogen are fcc and hcp hollow sites on the surface. The calculated adsorption energies vary between $-1$ eV for $\theta_{\text{Cl}} = \theta_{\text{H}} = 0.11$ up to $-0.5$ eV for for $\theta_{\text{Cl}} = \theta_{\text{H}} = 0.44$. Configurations with $\theta_{\text{Cl}} = \theta_{\text{H}} > 0.44$ were found to be unstable. Obviously, a repelling interaction between the adsorbed atoms leads to a weakening of the adsorption strength. According to a Bader charge analysis, adsorbed chlorine as well as hydrogen are negatively charged. The calculated adsorption energies of individual species have been found to be $-0.23$ eV and $-1.79$ eV for H and Cl, respectively. These energy values are in good agreement with previous DFT calculations. The mean adsorption energy of the coadsorbed state at a coverage of 2/9 (cf. diagram in Fig. 2) results practically as average of the individual adsorption energies.

**Comparison with experiments.**—On the basis of our coadsorption model introduced above, we have shown that the adsorption of the ions can be described by the standard Langmuir model with rescaled parameters. In this section, we will apply the proposed reduced model to the adsorption of chloride ions on copper in a highly acidic solution. As mentioned in the Introduction, this problem is of great importance for the electrochemical deposition of copper interconnects within the framework of the damascence technique. The adsorption of Cl and H on copper has been investigated in many studies, both experimentally...
Figure 2. Top views of stable atom configurations of different coadsorption states with equal coverages of chlorine and hydrogen (atom colors as in Fig. 1). The diagram shows the corresponding mean adsorption energy as a function of the total coverage $\Theta = \Theta_{Cl} + \Theta_{H}$. Additionally the adsorption energy of the individual species at a coverage of 2/9 is shown.

Figure 3. (a) Surface density $\Gamma_{Cl}^{eq}$ of chloride ions on copper as a function of the bias potential of the copper electrode for different chloride concentrations $c_{Cl}$ in the bulk solution. Reproduced from data in Fig. 2 of Ref. 18 (b) Representation of the linear dependence of $1/\Gamma_{Cl}^{eq}$ on $1/c_{Cl}$ for the data in (a) for bias potentials $E_{SHE} = -0.4$ up to 0.2 V (from top to bottom).

Figure 4. Saturated surface density of chloride ions $\Gamma_{Cl}^{S}$ as a function of the bias potential $E_{SHE}$. The solid symbols result from an extrapolation of the linear fits of the data in Fig. 3b. The curve represents a fit to the sigmoid function in Eq. 33.

and theoretically, see e.g. $^{35-39}$ To our knowledge, there are only few experiments concerning the quantitative determination of the Cl coverage on copper. Here, we employ experimental findings obtained by Horanyi et al., using the radio-active method.$^{18}$ As shown in Fig. 3a, the surface density of chloride on copper depends on the bias potential as well as on the chloride concentration in the bulk solution. In this work, the potential is referred to the standard hydrogen electrode (SHE). In the literature, the adsorption of chloride ions in an acidic solution is often described by the common Langmuir model for a single species without explicit consideration of the presence of hydrogen ions. The corresponding equilibrium surface density is given by formula 19 with $A \rightarrow Cl$

$$\frac{1}{\Gamma_{Cl}} = \frac{1}{\Gamma_{Cl}^{eq}} + \frac{1}{\Gamma_{Cl}^{S}} \frac{c_{Cl}}{c_{Cl} + \chi}$$  \[29\]

This equation reveals the linear dependence of $1/\Gamma_{Cl}^{eq}$ on $1/c_{Cl}$. The measurement data in Fig. 3a roughly show such a linear dependence as can be seen from the plots in Fig. 3b with the bias potential as curve parameter. By fitting the data in Fig. 3b to a linear function

$$1/\Gamma_{Cl}^{eq} = 1/\Gamma_{Cl}^{eq}_{0} + \gamma$$

...
A→Cl and B→H, we find
\[ \hat{\Gamma}^S_{Cl} = \Gamma^S_{Cl} = \frac{1 + (1 - \alpha)k_H c_H}{1 + (1 - \alpha)K_H c_H} \Gamma^0_{Cl} \]  
[30]

Determination of all unknown parameters in Eq. 30 at once by fitting the potential dependence of the data in Fig. 4 was not unique. However, in all cases we found that the value of α was almost one. With α = 1, Eq. 30 simplifies to

\[ \hat{\Gamma}^S_{Cl} = \frac{\Gamma^0_{Cl}}{1 + (1 - \beta)K_H \exp(-B_H E) c_H} \]  
[31]

Using the general formula 27, we obtain the following potential dependence of \( \hat{\Gamma}_{Cl} \)

\[ \hat{\Gamma}^S_{Cl} = \frac{\Gamma^0_{Cl}}{1 + \frac{1}{\chi} \exp(-B_H E) c_H} \]  
[32]

Since for positive bias potential \( E \), chloride adsorption is more favorable than hydrogen adsorption, we expect \( B_H > 0 \). Then, the saturation surface density as a function of the potential represents a sigmoid function with \( \hat{\Gamma}^S_{Cl} = \Gamma^n_{Cl} \) for \( E \to +\infty \) and \( \hat{\Gamma}^S_{Cl} = 0 \) for \( E \to -\infty \). By introducing a critical bias potential \( E^* \), via the equation \( (1 - \beta)K_H c_H = \exp(B_H E^*) \), the chloride saturation density can be expressed as

\[ \hat{\Gamma}^S_{Cl} = \frac{\Gamma^0_{Cl}}{1 + \exp(-B_H (E - E^*))} \]  
[33]

Fit of the data points in Fig. 4 to Eq. 33 yields the solid curve in Fig. 4. The corresponding parameter values are \( \Gamma^0_{Cl} = 3.21 \times 10^{-6} \) mol/cm², \( B_H = 6.66 \) V⁻¹ and \( E^* = -0.226 \) V.

In the linear relationship \( 1/\hat{\Gamma}^S_{Cl} = 1/\Gamma^S_{Cl} + \chi/\Gamma^S_{Cl} \) between \( 1/\hat{\Gamma}^S_{Cl} \) and \( 1/\Gamma^S_{Cl} \), we have introduced the parameter \( \chi = 1/(\hat{\kappa}_{Cl} \Gamma^S_{Cl}) \) (compare Eq. 29). The fit of this parameter is presented in Fig. 5a as a function of \( 1/\Gamma^S_{Cl} \). Together with the derived dependence of the saturation surface density on the bias potential in Fig. 4, it is possible to derive the value of \( \hat{\kappa}_{Cl} \) as a function of the potential. The corresponding data points are shown in Fig. 5b. According to the general formula 22 derived above and considering the fit result \( \chi = 1 \), the ratio \( \hat{\kappa}_{Cl} \) is given by

\[ \hat{\kappa}_{Cl} = \frac{1 + (1 - \beta)K_H c_H}{1 + \hat{\kappa}_{H} c_H} \]  
[34]

By inserting the potential dependence introduced in Eq. 27, we find

\[ \hat{\kappa}_{Cl} = \frac{1 + (1 - \beta)K_H \exp(-B_H E) c_H}{1 + K_H \exp(-B_H E) c_H} \frac{\Gamma^0_{Cl}}{\hat{\kappa}_{Cl} \exp(-B_H E c_H)} \]  
[35]

Because of a considerable scatter of the data points in Fig. 5b, a general fit of all unknown parameters in Eq. 35 is unreliable. Thus, in a rough manner, we approximated the prefactor in front of \( K_{Cl} \) by \( \exp(-B_H E c_H) \). This corresponds to the limiting case \( \beta = 0 \) in Eq. 35 and yields a lower estimate of the parameter \( B_{Cl} \). As a consequence the dependence of \( \hat{\kappa}_{Cl} \) on the hydrodynamic bulk concentration cancels. The fit results read then \( B_{Cl} = -1.4 \) V⁻¹ and \( K_{Cl} = 125 \) m³/mol. The corresponding value of the charge transfer for chloride adsorption is \( \Delta z = 0.036 \) e. For comparison, Foresti et al. studied the adsorption of chloride ions on the Ag(111) surface and found a partial charge transfer of 0.07 e (see Tab. 1 of Ref. 34). As a tendency, with increasing value of \( \beta \), our fit suggests a weaker exponential potential dependence of the parameter \( \hat{\kappa}_{Cl} \) since then the magnitude \( |B_{Cl}| \) decreases.

In summary, the above analysis of the measurements of the adsorbed chloride surface density by Horanyi et al. provides us with the following basic data to predict the chloride equilibrium coverage. The potential dependence of the saturated surface concentration \( \Gamma^S_{Cl} \) is given by Eq. 33 and that of the ratio of the adsorption and desorption rate by \( \hat{\kappa}_{Cl} = K_{Cl} \exp(-B_{Cl} E) \). The corresponding parameter values \( K_{Cl}, B_{Cl}, \Delta z, \Gamma^0_{Cl}, B_{Cl}, \) and \( E_0 \) are listed in Table I. With these data, the chloride equilibrium surface density was calculated according to model Equation 29 as a function of the electrode potential for different chloride concentrations in the bulk solution. As can be seen in Fig. 6a, the simulation results agree very well with the measurements. We calculated the equilibrium surface densities also for bulk concentrations higher than in the experiments. For \( c_{Cl} = 1 \) mM and 10 mM, the equilibrium surface density \( \hat{\Gamma}^S_{Cl} \) is very close to the saturation value \( \hat{\Gamma}^S_{Cl} \). Increasing the chloride bulk concentration beyond 1 mM practically has no influence on the equilibrium surface density of chloride in the studied potential regime.

For comparison, we also studied a simplified adsorption model without consideration of a potential dependence of the saturation value of the surface density \( \hat{\Gamma}^S_{Cl} \), similar to approaches in Refs. 9–11,18–20. Because of our approximation \( \beta = 0 \), in Eq. 35, this corresponds to the limiting case of complete absence of adsorbed hydrogen. Fit of the measurements in Fig. 6a for a special bulk concentration, say \( c = 0.1 \) mM, yields the parameters \( \hat{\Gamma}^S_{Cl} = \Gamma^0_{Cl} = 3.21 \times 10^{-10} \) mol/cm² and \( B_{Cl} = 5.5 \) V⁻¹. The corresponding charge transfer during the adsorption process becomes 0.14 e. With these parameter values, the surface density of adsorbed chloride can be calculated for other bulk concentrations. As shown in Fig. 6b, there is a

**Table I. Model parameters for chloride adsorption in Fig. 6.**
considerable disagreement between simulation and measurements. This clearly demonstrates the importance of including the potential dependence of the saturation surface density $\Gamma^0(E)$ in the model description of chloride adsorption in an acidic solution.

Conclusions and Discussion

We proposed a simple mechanistic model of the coadsorption of two ion species in aqueous solution on an electrode surface, where the mutual interaction of the adsorbed species was phenomenologically expressed by two model parameters $\alpha$ and $\beta$. The meaning of these parameters was illustrated for special cases. Determination of the equilibrium surface densities of the two ion species in the coadsorbed state revealed that the the equilibrium density of one species can be expressed in form of the common Langmuir isotherm with modified model parameters depending on the concentration of the second species and the electrode potential. As one result, we found how the saturation surface density of one species in the limiting case of high bulk concentration of this species depends on the electrode potential.

Our model approach was applied to the $\text{Cl}^-\text{H}^+$-coadsorption on copper because of its importance for the electrochemical deposition of copper. DFT calculations for this system showed that hydrogen is able to replace adsorbed chlorine atoms of a pure copper chloride adlayer. Calculated mean adsorption energies for several surface structures of coadsorbed chloride and hydrogen were in the range from $-1.0$ to $-0.5$ eV, depending on the total coverage of both species. These DFT results suggest that the presence of hydrogen should considerably affect the adsorption of chloride.

Model parameters of our phenomenological coadsorption model were estimated by comparing with radiotracer measurements of the chloride adsorption on a porous copper electrode in an acidic medium reported in Ref. 18. Those measurements suggest a potential dependence of the saturation surface density of chloride in the limit of large chloride bulk concentration as also predicted by our model. The corresponding model parameters describing this potential dependence could be fitted. A fit of the potential dependence of the kinetic parameter $k_{\text{Cl}}^0/k_{\text{Cl}^-}$ was only approximately possible because of the scatter of data. To improve the parameter fit, further measurements of the chloride adsorption on copper in an acidic medium with different pH values are desirable. Furthermore, we note that the absorption of hydrogen in subsurface sites could significantly influence coadsorption (cf. for example Ref. 19). The present model of the $\text{Cl}^-\text{H}^+$-coadsorption together with a refined fitting of the model parameters could be helpful in the modeling of the complex process of electrochemical copper deposition in the presence of additives.

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