

# Cl electrosorption on Ag(1 0 0): Lateral interactions and electrosorption valency from comparison of Monte Carlo simulations with chronocoulometry experiments

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## Abstract

We present Monte Carlo simulations using an equilibrium lattice-gas model for the electrosorption of Cl on Ag(1 0 0) single-crystal surfaces. Fitting the simulated isotherms to chronocoulometry experiments, we extract parameters such as the electrosorption valency  $\gamma$  and the next-nearest-neighbor lateral interaction energy  $\phi_{\text{nnn}}$ . Both coverage-dependent and coverage-independent  $\gamma$  were previously studied, assuming a constant  $\phi_{\text{nnn}}$  [I. Abou Hamad, Th. Wandlowski, G. Brown, P.A. Rikvold, J. Electroanal. Chem. 554–555 (2003) 211]. Here, a self-consistent, entirely electrostatic picture of the lateral interactions with a coverage-dependent  $\phi_{\text{nnn}}$  is developed, and a relationship between  $\phi_{\text{nnn}}$  and  $\gamma$  is investigated for Cl on Ag(1 0 0).

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## 1. Introduction

Studies of lateral interactions between adsorbed particles are motivated by the need to understand the origin of the wide variety of ordered overlayers and phase transitions at fractional adsorbate coverage on metal surfaces. These interactions have contributions ranging from short-range and van der Waals to long-range dipole–dipole, and lattice-mediated interactions [1]. Hard-square short-range interactions and dipole–dipole long-range interactions are the major contributions to the lateral interactions for bromine adsorption on Ag(1 0 0) [2]. In this paper, we explore the validity and applicability of such a model for adsorption of chlorine on Ag(1 0 0).

Halide electrosorption on single-crystal metal electrode surfaces is a good model system for studying the properties of the electrode–electrolyte interface in an electrochemical cell. Due to its relative simplicity, it can be used to distinguish between the various contributions of different parameters according to the effect of their inclusion on the overall behavior of the system. A mean-field approach is not sufficient, even for the description of one of the simplest halide–electrosorption systems Br/Ag(1 0 0). However, a simple lattice-gas model with constant parameters is sufficient to describe its equilibrium [2,3] and dynamic [4] properties. While the electrosorption of Br on single-crystal Ag(1 0 0) from aqueous solution has been extensively studied as an example of adlayer formation in an electrochemical system [2,5–8], less attention has been given to the electrosorption of Cl [3,9,10] on Ag(1 0 0). A lattice-gas model with constant parameters is not sufficient to describe Cl/Ag(1 0 0);

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therefore, this system can be used to further investigate the nature and characteristics of the lateral interactions between the adsorbed halide atoms. In particular, we here develop a self-consistent picture of variable lattice-gas parameters based on the resident charge on the adatoms being coverage-dependent or electrode potential-dependent (through the coverage).

The rest of this paper is organized as follows. In Section 2, we describe an electrostatic model of the adlayer that is used in the simulations, the lateral interaction energies, and the Monte Carlo methods used. A brief description of the experimental procedure is given in Section 3. The results of fitting the simulations to experimental data are detailed in Section 4, followed by a brief comparison with Br/Ag(1 0 0) in Section 5. Our conclusions are summarized in Section 6.

## 2. Self-consistent electrostatic adlayer model

### 2.1. Lattice-gas model

The adsorption of Cl ions occurs at the four-fold hollow sites of the Ag(1 0 0) surface [11], which form a square lattice as shown in Fig. 1. To approximate the equilibrium behavior of this system, we use a lattice-gas model, in which the lattice sites correspond to the adsorption sites. Mitchell et al. [12] used an off-lattice model for the Br/Ag(1 0 0) system to show that the Br adsorbates spend most of the time near the four-fold hollow sites of the Ag(1 0 0) surface, thus justifying the lattice-gas treatment of halide adsorption. To describe the energy associated with a configuration of adsorbates on the surface, a grand-canonical effective Hamiltonian [2,6,13,14] is used,

$$\mathcal{H} = - \sum_{i<j} \phi_{ij} c_i c_j - \bar{\mu} \sum_{i=1}^N c_i, \quad (1)$$

where  $\sum_{i<j}$  is a sum over all pairs of sites,  $\phi_{ij}$  are the lateral interaction energies between particles on the  $i$ th and  $j$ th lattice sites, measured in meV/pair,  $\bar{\mu}$  is the electrochemical potential, measured in meV/particle, and  $N = L^2$  is the total number of lattice sites. The local occupation variable  $c_i$  is 1 if site  $i$  is occupied and 0 otherwise.

The long-range interactions,  $\phi_{ij}$ , depend on the distance,  $r_{ij}$ , between ions  $i$  and  $j$  (measured in Ag(1 0 0) lattice spacing units,  $a = 2.889 \text{ \AA}$  [7]) as

$$\phi_{ij} = \begin{cases} -\infty & r_{ij} = 1 \\ \frac{2^{3/2} \phi_{nm}}{r_{ij}^3} & r_{ij} \geq \sqrt{2} \end{cases}, \quad (2)$$

where the infinite value for  $r_{ij} = 1$  indicates nearest-neighbor exclusion, and negative values of  $\phi_{ij}$  denote long-range repulsion. The coverage-isotherms were simulated using a square  $L \times L$  lattice with periodic boundary conditions to reduce finite-size effects.

The electrochemical potential  $\bar{\mu}$  is related to the bulk ionic concentration  $C$  and the electrode potential  $E$  (measured in

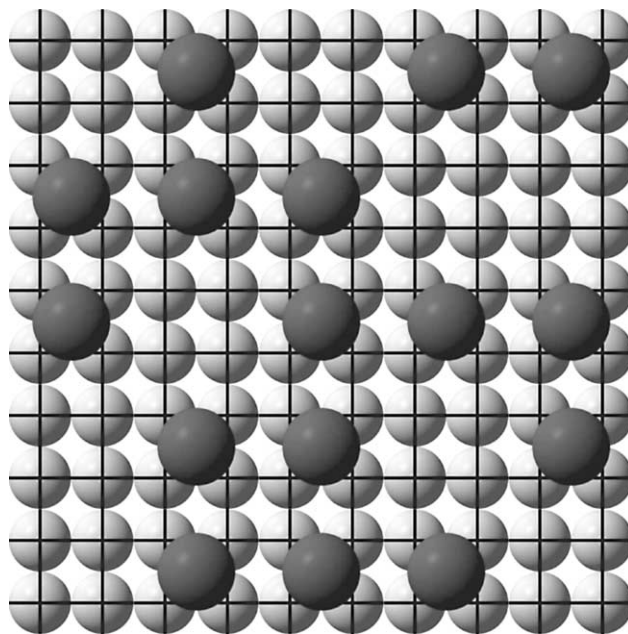


Fig. 1. Cl (larger, dark gray, spheres) adsorbed at the four-fold hollow sites of the (1 0 0) surface of Ag (smaller, lighter gray, spheres). The grid frame corresponds to the lattice of adsorption sites. The figure is drawn approximately to scale.

mV). In the dilute-solution approximation, the relationship is

$$\bar{\mu} = \bar{\mu}_0 + k_B T \ln \left( \frac{C}{C_0} \right) - e \int_{E_0}^E \gamma(E') dE', \quad (3)$$

where  $\bar{\mu}_0$  is an arbitrary constant,  $C_0$  is a reference concentration (here taken to be 1 mM), and  $e$  is the elementary charge unit [15]. The reference potential  $E_0$  is chosen sufficiently negative such that the coverage vanishes at  $E_0$  for all values of  $C$  used, and  $\bar{\mu}$  has the sign convention that  $\bar{\mu} > 0$  favors adsorption. The relationship between  $\bar{\mu}$ ,  $C$ , and  $E$  is discussed further in the Appendix A.

### 2.2. Lateral interaction energies

When Cl ions adsorb on the surface, a fraction of their charge is transferred through the external circuit. This fraction,  $\gamma e$ , is negative and is directly related to the average resident charge per ion,  $q = -(1 + \gamma)e$  [16]. This relationship is an approximation and is more valid as the potential at the adsorbate approaches the value of the potential in the solution. For the current system's ionic strength, this condition is only approximately satisfied and may be considered as a source of error.

We have previously shown [3] that for Cl/Ag(1 0 0), the electrosorption valency  $\gamma$  depends on the coverage  $\theta$ , which is defined as

$$\theta = N^{-1} \sum_{i=1}^N c_i. \quad (4)$$

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