

Why Silver Deposition is so Fast: Solving the Enigma of Metal Deposition**

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The international Ampere, which was the accepted unit of current until 1948, was defined as that unvarying current that would deposit 0.001118000 g of silver from a solution of silver nitrate in water. Silver deposition was chosen to define the standard because it is fast and reproducible, and because its equilibrium potential is far from the hydrogen or oxygen evolution regions. In fact, the elementary deposition step: $\text{Ag}^+ + e^- \rightleftharpoons \text{Ag}$ is so fast that its rate constant has not yet been determined. Faraday could have saved a lot of time if he had studied silver deposition instead of the sluggish evolution of gases.

At a first glance it is surprising that silver deposition is so fast: The energy of hydration of the silver ion is about 5.15 eV, and it would be expected to lose a large part of its solvation shell when it approaches the electrode surface, so that the corresponding energy of activation should be a sizable fraction of its solvation energy: somewhere between 1–3 eV. The same argument holds for the deposition of all common metal ions. Univalent ions typically have solvation energies of the order of 5 eV, divalent ions of 20 eV, and for trivalent ions the situation is even worse. To some extent, the electrostatic image interaction of the ion with the metal should aid the approach to the surface, but at distances at which the solvation shell breaks up the image energy is much smaller

than the solvation energy. So how do these ions ever come close enough to the electrode surface to become discharged and incorporated into the metal? This problem has been aptly named the “enigma of metal deposition”.^[1]

Because of its interesting properties, we have performed a theoretical investigation of silver deposition as a prototype for the deposition of monovalent ions; in the following we present our results, which are based on a combination of molecular dynamics, density functional (DFT) calculations, and a theory developed in our own group. First we shall discuss, how the solvated silver ion approaches the silver electrode, then we present the electronic interaction of the silver 5s orbital with the silver electrode, and finally we shall use these results to calculate the free energy surface for the deposition. All technical details are provided in the Supporting Information.

Experimentally, the mechanism of silver dissolution and deposition was elucidated in the 1950s by Gerischer,^[3] who showed that the first and rate-determining step in the dissolution is the detachment of a silver atom from a kink site onto a terrace. The subsequent dissolution, namely $\text{Ag}(\text{terrace}) \rightarrow \text{Ag}^+ + e^-$ is so fast that it is in equilibrium.

A central question in the deposition or the adsorption of ions from solution is: What happens to the solvation sheath as the ion approaches the surface? Does it have to overcome an energy barrier to shed its solvation shell before it is deposited? The first article to investigate this problem was published by Pecina et al.,^[4] who studied the adsorption of an iodide ion on Pt(100). The relevant quantity is the potential of mean force (PMF) for the ion to move from the interior of the solution towards the surface. This potential was calculated by umbrella sampling techniques based on a classical molecular dynamics simulation employing a suitable force field. For the I^- ion, the potential of mean force rises rapidly as it moves from the bulk of the aqueous solution towards the surface, reaching a value of about 1.35 eV (see Figure 1). Thus, this ion loses about half its solvation energy (about 2.5 eV), as would be expected from simple geometric considerations.

However, the situation for the Ag^+ ion is completely different: Here the potential stays almost constant as the ion moves towards the surface, and even reaches a shallow minimum near 2.9 Å. A closer investigation shows that in this position the silver ion is surrounded by a stable sheath of water molecules providing a very effective solvation cage (see the Supporting Information). We stress that this potential includes only the interaction with the water, not with the electrode. Thus, in this configuration the role of the electrode is indirect: it helps to fix the water molecules in the optimum position to form the solvation sheath.

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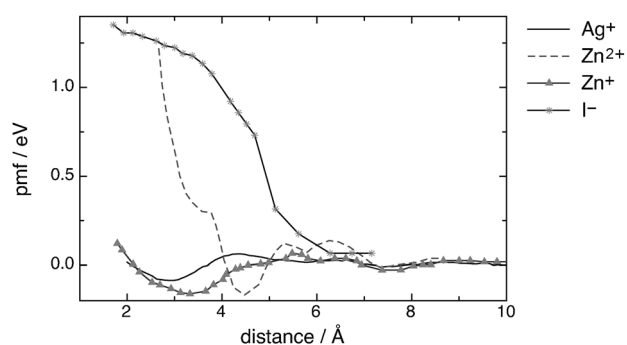


Figure 1. Potentials of mean force (PMF) for the approach of ions to move from the bulk of an aqueous solution towards an electrode surface: Ag^+ towards a $\text{Ag}(100)$, Zn^+ and Zn^{2+} towards $\text{Zn}(0001)$, and I^- towards $\text{Pt}(100)$. The potential refers only to the interaction of the ions with the solvent. The data for Zn deposition were taken from Ref. [5], those for the iodide ion from Ref. [4].

Exactly the same effect had been observed before by Pecina and Schmieckler for the Zn^+ ion,^[5] the PMF of which is also shown in Figure 1. Similarly, Eck and Spohr^[6] observed in their simulations that Li^+ ions have a stable configuration very close to a mercury electrode.

The more strongly solvated divalent Zn^{2+} ion also shows a minimum in the PMF, but at a larger distance from the surface, where its two primary solvation sheaths are still intact. At shorter distances, where it has to shed its secondary sheath, its potential starts to rise steeply. Cu^+ and Cu^{2+} , which we have also investigated, behave very similarly to zinc. For reasons of clarity we have not included these data in the Figure.

Thus, in the cases investigated here or in the literature, small univalent metal ions can get very close to the electrode surface without losing solvation energy. In contrast, the potential of mean force of bigger anions or of divalent ions rises steeply as they approach the surface. The small univalent metal ions fit neatly into the water structure at the surface, while the larger anions do not.

To study the electronic interaction of the $\text{Ag}5s$ orbital with a silver surface, we have investigated the energy of a silver atom near a $\text{Ag}(100)$ surface as a function of the distance. The atom adsorbs at a hollow site at a distance of 1.88 Å measured from the center of the top layer of $\text{Ag}(100)$ atoms, with an energy of adsorption of -2.46 eV with respect to the vacuum. To understand the details of the interaction, we have calculated the density of states (DOS) of the $5s$ orbital for the Ag atom as it approaches the surface; the corresponding plot is shown in the Supporting Information.

From these DOS we evaluated the coupling constants, or rather their square $|V|^2$, of the $5s$ orbital with the sp and with the d band of silver (see the Supporting Information). The coupling to the d band is very small, but the interaction with the sp band is very strong and long-range, and reaches a value of about 7 eV² close to the surface where the deposition takes place. To give a comparison, hydrogen adsorption on Pt is immeasurably fast, and is catalyzed by the interaction of the $\text{H}1s$ orbitals with the $\text{Pt}d$ band. But even in the adsorbed state, the coupling $|V|^2$ of hydrogen with the d band is only

about 3.9 eV².^[7] We shall show below that this strong and long-range interaction is one of the factors that make silver deposition and dissolution so fast.

The experimental results by Gerischer^[3] show that the rate-determining step in the dissolution is the detachment of a silver atom from a kink site onto the terrace. This occurs without electron transfer, and can be evaluated by standard DFT. According to our calculations, on the $\text{Ag}(100)$ surface the energy of a silver atom adsorbed on the terrace is $\Delta E = 0.28$ eV higher than for the kink site; the energy of activation for the detachment from the kink is $\Delta E^\ddagger = 0.57$ eV. Gerischer obtained the corresponding Gibb's free energies, and his values are for a polycrystalline surface, namely $\Delta G = 0.45$ eV, and $\Delta G^\ddagger = 0.58$ eV. The agreement in the activation energies is very satisfying, the small difference in the reaction energy can easily be explained by the difference in the surface structure and by the entropy term, which is missing in our calculations. For more information about the diffusion of silver atoms on a silver surface see Refs. [10,11] and references therein.

With the information from the calculations presented above, we are able to calculate the free energy surface for the deposition/dissolution of silver in aqueous solutions. Our calculations are based on our own theory, which combines ideas of the Marcus^[8] and Hush^[9] theories with those of the Anderson–Newns model.^[12,13] Detailed information is provided in the Supporting Information. Here, we briefly discuss the concept of the solvent coordinate, which plays a central role in electron-transfer theory. In the deposition of a silver ion, the initial state is a fully solvated ion sitting in the minimum of the PMF curve in Figure 1. The final state is an atom deposited on the terrace, which interacts only weakly with the solvent. For the reaction to occur, the solvent configuration must fluctuate and assume an intermediate configuration in which an electron transfer happens and the ion is discharged. The configurations of the solvent can conveniently be described by the solvent coordinate introduced by Hush. In our representation it is normalized in such a way that a solvent coordinate q describes a solvent configuration that would be in equilibrium with a reactant of charge $-q$.^[14] Thus, during silver deposition the solvent coordinate passes from -1 to 0 .

As the solvent fluctuates, the occupation of the valence orbital changes and assumes fractional values. From DFT we can obtain the energy of neutral atom as a function of the distance and, with some tricks,^[2,15] that of ions with integral charges. We compare these energies with those obtained from our model and correct for the many-body terms missing in the Anderson–Newns theory (for details, see Ref. [2] and the Supporting Information). We can then calculate the free energy surface for the reaction as a function of the position of the reactant and the solvent coordinate q .

Figure 2 shows the surface for the deposition/dissolution of a Ag^+ ion. Our theory allows calculations for a specified electrode potential, and this surface is for the case where the ion in the bulk of the solution is in equilibrium with the kink site, which defines the equilibrium potential for the overall reaction. As the energy of the atom adsorbed on the terrace is higher than that of a kink atom, the deposition is uphill by

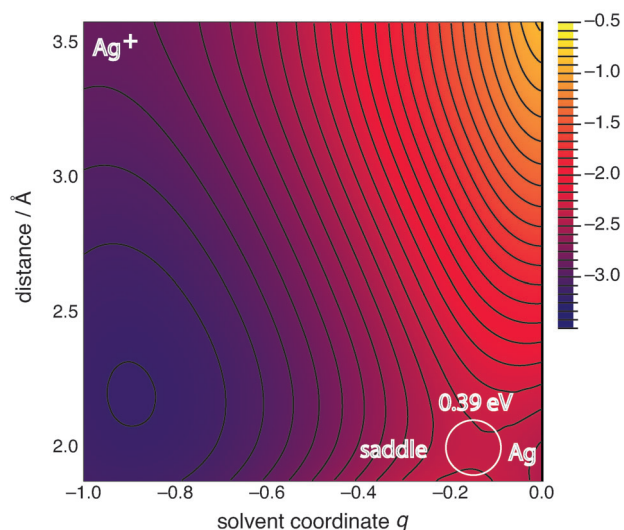


Figure 2. Free energy surface for the deposition of silver as a function of the distance from the electrode and the solvent coordinate q . The calculations have been performed for the equilibrium potential of the overall reaction, that is, for equilibrium with a kink site. All energies are in eV.

0.28 eV. The free energy at large distances and $q = -1$ corresponds to the Ag^+ ion. There is a local minimum centered near $q = -1$ and $d = 2.3 \text{ \AA}$, which is induced by the minimum in the PMF observed in Figure 1; the interaction with the silver electrode has shifted the minimum closer to the surface. At $q = 0$ and short distances the surface exhibits a shallow minimum for the deposited atom. The saddle point for the deposition is close to the minimum for the deposited atom. This is in line with the idea expressed by Gileadi,^[1] that is, it is the ion that transfers through the larger part of the double layer. The energy of activation for the deposition is about 0.39 eV; for the reverse direction, the dissolution, it is 0.11 eV. The saddle point is so close to the surface because the ion does not lose solvation energy during its approach. Its position at a solvent coordinate near $q = -0.18$, that is, close to the final state, is due to the fact that the reaction is uphill, and is in line with the expectations of Marcus theory. As mentioned above, the energy of activation for the detachment of a silver atom from a kink site is 0.57 eV and thus higher than that for silver dissolution, in agreement with the findings of Gerischer.^[3]

The central question of our investigation was: Why is silver deposition so fast, even though the ion loses more than 5 eV of solvation energy in the process? The explanation lies in the combination of two effects: 1) Like several other univalent metal ions, the Ag^+ ion can get very close to the electrode surface without losing solvation energy. There is even a minimum in the potential of mean force when the ion is in a position very close to the surface, where it has a firm solvation shell stabilized by the electrode surface. In this position, the ion is close enough to the surface to experience the electronic interaction with the silver electrode; 2) The interaction of the silver 5s orbital with the sp band of silver is very strong and long-range. This is understandable, as the

approaching reactant interacts with identical atoms on the surface, which is energetically favorable. Furthermore, the 5s orbitals are large, which increases the overlap and extends the range of the interaction.

We surmise that the deposition of small univalent metal cations is always fast. In the four cases investigated so far, namely Ag^+ , Zn^+ , Li^+ , Cu^+ , the ions can approach very close to the surface without loss of solvation energy. Furthermore, the electronic overlap of a metal ion with metal atoms of the same kind should always be favorable. So the deposition of these ions is not governed by d-band catalysis, but by sp-band autocatalysis. The same holds for the reverse directions, namely metal dissolution. Therefore our findings imply that corrosion is much faster than expected from simple arguments.

What about multivalent ions? Marcus theory suggests that their deposition or dissolution should involve a series of one-electron steps, as the reorganization energies for the simultaneous transfer of two electrons are typically four times higher. Furthermore, these ions cannot get close to the surface without losing their secondary solvation sheath, which costs energy. For Zn^{2+} and Cu^{2+} we have already shown that the potential of mean force rises steeply as the ion approaches the surface (see Figure 1 and Ref. [5]), and we may conclude that the transfer indeed occurs in two steps. This suggests that the deposition of multivalent ions occurs in a series of one-electron steps, and only in the last step the ion is deposited onto the electrode; mutatis mutandis this should hold also for metal dissolution.

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