Spiral Adsorbate Structures on Monoatomic Nanowire Electrodes

Stefan Frank,[b] Christoph Hartnig,[b] Axel Groß,[a] and Wolfgang Schmickler*[a]

Monoatomic nanowires embedded in an electrolyte solution can be considered as one-dimensional electrodes. In order to investigate the interaction of the wire with the solution, classical molecular dynamics simulations are performed for a silver wire surrounded by an aqueous solution of NaCl. The required interaction potentials are obtained from ab initio calculations. An uncharged wire is covered by an ordered adsorbate structure, which consists of intertwined strands of Cl^- and Na^+ ions that wind around the wire. This is in striking contrast to plane silver electrodes, at which Na^+ ions do not adsorb at all. The difference in the adsorption behavior between monoatomic and plane electrodes is mainly caused by steric effects. Our findings suggest that the distinction between non-adsorbing and adsorbing ions, on which our understanding of the adsorption of bulk electrodes is based, does not hold for monoatomic wires.

Nanowires are a highly popular area of research. This great interest is driven both by the new physical phenomena that occur at wires with diameters of a few atomic radii, and by their possible applications in nanotechnology. Naturally, the limit of monoatomic wires deserves special attention, and much research effort has been focused on their physical properties. Electrochemistry offers convenient methods for the generation of such monoatomic nanowires.[1, 2] Experimental investigations of these wires have mainly dealt with their conductivity, and their elasticity[3, 4]—properties which are also investigated for wires in air or vacuum. However, monoatomic wires embedded in a solution can be considered as one-dimensional electrodes. Thus, the question if, and how, their properties differ from those of bulk electrodes is of obvious importance. Recently, Leiva et al.[5] have shown that the capacity of these wires is substantially enhanced, and that the transport towards and away from these wires is faster by orders of magnitudes, compared to bulk electrodes. In addition, the potential of zero charge of gold and silver wires was shifted substantially towards more positive values.

Herein, we focus on another fundamental property of electrochemical nanowires, namely their interaction with a surrounding electrolyte solution, especially with ions. At bulk electrodes, ions shed off a large part of their solvation shell during adsorption; therefore the adsorption of simple ions is governed by their solvation. Small, strongly solvated cations like Na^+ or K^+ do not adsorb at all. In contrast, practically all simple anions like Cl^- or Br^- adsorb at uncharged or positively charged electrodes, because their energy of solvation is substantially lower than that of cations with a similar size. For steric reasons, ions that are adsorbed on a monoatomic wire lose only a small part of their solvation shell. Therefore, we may expect that the energy of activation for adsorption is reduced. In order to explore the adorption of ions on nanowires quantitatively, we perform a theoretical study based on ab initio calculations combined with molecular dynamics. Our results indicate that, in contrast to flat electrodes, all ions adsorb on a nanowire. Furthermore, we propose the existence of a one-dimensional salt-like spiral if the nanowire is exposed to an aqueous solution, a structure that has never been observed or suggested on electrodes before.

As our model system, we choose a monoatomic silver wire in contact with an aqueous solution of NaCl, and study its statistical mechanics by molecular dynamics simulation. The choice of the electrolyte is governed by the fact that the two kinds of ions exhibit contrasting adsorption behavior at bulk electrodes.

Computer simulations require good interaction potentials, if the results are to be meaningful. There are well-tested potentials for bulk silver in contact with aqueous solutions,[6, 7] but the interactions of particles with a monoatomic wire may differ from those with a flat electrode surface. Therefore, as a first step, we calculate the interaction potential of a silver wire with water, Na^+ and Cl^- anew.

For this purpose, we first determine the structure of a monoatomic silver wire itself, and perform DFT calculations for a ring of Ag atoms. The ring is chosen instead of a linear wire to avoid edge effects. We use the B3LYP hybrid exchange-correlation functional[8] and the LANL2MB atom-centered basis set.[9, 10] The ring consists of 30 atoms, as the energy per atom converges for this number of atoms. The optimized Ag—Ag distance of 2.74 Å shows a contraction of the Ag—Ag bond compared to the metal crystal (2.89 Å). This is in qualitative agreement with the results of Leiva et al.,[5] though our interatomic distances are a little larger than theirs. This interatomic distance is kept constant in all other calculations, and in particular in the molecular dynamics simulations.

The interaction potential between the wire and the ions is then obtained by first calculating the image potential, as this gives the interaction potential at large distances. The image potential is calculated from standard electrostatics, treating the wire as a conducting cylinder. At short distances, the ions are adsorbed and partially discharged. The energies of the adsorbed, partially charged atoms can be calculated by DFT; we

[a] Prof. Dr. A. Groß, Prof. Dr. W. Schmickler
Institut für Theoretische Chemie
Universität Ulm, 89069 Ulm (Germany)
Fax: (+49) 731-502-2819
E-mail: wolfgang.schmickler@uni-ulm.de

[b] Dr. S. Frank, Dr. C. Hartnig
Zentrum für Sonnenenergie- und Wasserstoff-Forschung
Baden-Württemberg 89081 Ulm (Germany)

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/cphc.200700822.

These are not the final page numbers! ↗↗

do this both for the bridge and the on-top sites of the wire, at the equilibrium distance and at a few distances in the direct vicinity. These calculations give the energy of adsorption as the difference between the energy of an atom at infinity and the adsorbed, partially charged, atom. However, in our case the reference state is an ion at infinity. As has been discussed by Koper and van Santen,[11] the adsorption energy for a cation is obtained by adding the energy of ionization of the atom and subtracting the work function of the wire, thus accounting for the transfer of an electron to the wire. Correspondingly, for an anion, one subtracts the electron affinity of the atom and adds the work function. In this way, we obtain the interaction potentials at short distances both for the bridge and the on top sites (see Table 1), which are then joined smoothly to the

---

Table 1. Adsorption energy E_{ad} and equilibrium distance d of single ions, measured from the center of the wire.

	Na$^+$ bridge	Na$^+$ on top	Cl$^-$ bridge	Cl$^-$ on top
E_{ad} [eV]	−2.22	−2.01	−3.39	−2.96
d [Å]	2.52	2.65	2.29	2.45

---

image potential. At large distances, these potentials are identical for bridge and on-top sites. For shorter distances, we interpolate the values for intermediate positions with a cosine function. Our value for the adsorption energy of Na$^+$ is within the same range as the values that can be derived from the work of Karttunen and Pakkanen[18] for Ag clusters of various sizes. In contrast, our adsorption energy for Cl$^-$ is somewhat lower than the value of 4.47 eV calculated by Koper and van Santen.[11] This could be due to the lower dimensionality of our system, in which an adsorbed Cl has fewer neighbors.

To obtain the interaction potential between the wire and water, we calculate the adsorption energy for a single water molecule at four particular configurations: on top and bridge sites, with the oxygen pointing towards the wire (dipole moment perpendicular to the wire), and with the molecule lying flat (dipole moment parallel to the wire). In each case we optimize both the geometry of the water and the distance to the wire. The resulting adsorption energies are shown in Table 2. Adsorption energies of water on Ag(111) calculated by other authors depend on the geometry and the method used,[12–14] and generally lie in the range between −0.18 to −0.35 eV. They all agree that the on-top site is the most favorable, and that there is a slight preference for the dipole
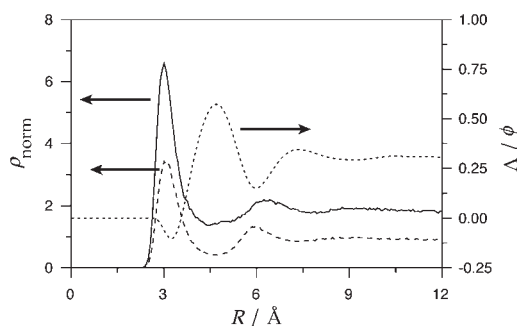
moment to point away from the surface. Our values lie towards the upper end of this range (weaker adsorption), which again could be due to the lower coordination. In addition, we perform calculations for a few intermediate geometries. We then construct a wire–water potential of the form suggested by Spohr et al.,[15] using the results of our calculations to determine the parameters of that potential. This is a pairwise potential, which introduces a certain error. However, the interaction of silver with water is much weaker than the water–water interaction. Therefore, at ambient temperatures, the structure of water at the surface does not depend critically on the details of the metal–water potential.

For the other interactions we use well-established potentials. For water, we use the Walbran model,[16] a polarizable extension of the Toukan–Rahman model,[17] and the water–ion potentials are taken from ref. [6]. The latter gives good values for the solvation energies of the ions.

With these potentials, we perform standard molecular dynamics simulations for the solution, keeping the silver wire fixed. At first we perform simulations for pure water with a silver wire consisting of 25 atoms centered at the z axis, surrounded by 1600 water molecules. The silver atoms are kept fixed at the positions of the bare wire. The box dimensions are $60 \times 60 \times 68.5$ Å^3, and periodic boundary conditions are applied in all three directions. A restraining cylindrical potential with a radius of 18 Å is employed to prevent water molecules from evaporating. We correct electrostatic long-range interactions using an Ewald-type summation. The temperature is set to 298 K using a Berendsen[21] thermostat. After equilibration, we simulate for about 200–400 ps, using a time step of 0.5 fs.

The structure of the water at the interface has a great effect on the adsorption, since the ions must displace water from the surface and simultaneously lose a part of their solvation shell. Therefore we first determine the structure in the absence of ions (see Figure 1). The particle densities for oxygen and water show large peaks right at the surface, and a smaller peak corresponding to a second water layer at a distance of about 6 Å. There is a slight preference for the oxygen to be closer to the wire. This is difficult to observe in the densities, but it manifests itself in a dipole potential, which oscillates at the surface and then reaches a constant value of about 300 mV in the

---

Table 2. Adsorption energy and equilibrium distance d, measured from the center of the wire, of a single water molecule for two distinct orientations. A: oxygen towards the center, dipole perpendicular to the wire, B: flat, dipole parallel.

	A on top	A bridge	B on top	B bridge
E_{ad} [eV]	−0.215	−0.168	−0.186	−0.182
d [Å]	2.61	2.90	2.86	3.02

Figure 1. Particle densities for hydrogen (——), oxygen (----), and the electrostatic potential (·····) as functions of the radial distance. The densities of oxygen and hydrogen are normalized to unity and two, respectively, in the bulk.

bulk. This orientation affects the adsorption process. Qualitatively, the water structure that we obtain does not differ significantly from that observed by other workers at bulk silver electrodes,[7,19] but our dipole potential drop is somewhat smaller.

The adsorption of ions is determined both by interaction with the metal and interaction with the solvent. The latter can be characterized by the potential of mean force (pmf), which an ion experiences at a given position due to its interaction with the solvent. We calculate the pmf by umbrella sampling techniques and the results are shown in Figure 2. The potential
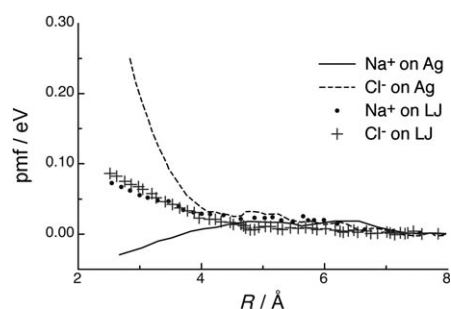
Figure 2. Potential of mean force for Na^+ and Cl^- ions near a silver (Ag) and a Lennard–Jones (LJ) wire.

of Na^+ is practically constant beyond a distance of 5 Å from the wire, and decreases slightly towards the surface. Obviously, the desolvation of the ion does not play a major role in the energetics. In contrast, the potential of Cl^- increases by about 0.3 eV as the ion moves from the bulk towards the surface. But even this increase is comparatively small compared to the solvation energy of Cl^- (ca. 3.2 eV). Both pmfs are in striking contrast to those of ions at flat electrodes, where they experience a barrier amounting to about half the energy of solvation,[20,22] which corresponds to a loss of about half of the solvation sheath. For steric reasons, this desolvation effect is much smaller on monoatomic wire electrodes. Indeed, quantitative evaluation shows that the solvation numbers of adsorbed Na^+ or Cl^- ions differ only by unity from the bulk value, so that a single ion loses only one water molecule from its solvation shell when it is adsorbed.

The difference in the shape of the potentials of mean force between the two ions must be caused by specific interaction with water. Water is preferentially adsorbed with its oxygen end towards the wire. The resulting negative excess charge in the vicinity of the wire attracts the positively charged Na^+ ions and repels the Cl^- ions. In order to verify this hypothesis, we also calculate the potential of mean force for a generic wire, which attracts water through a Lennard-Jones potential, but without any preference for either oxygen or hydrogen. As can be seen in Figure 2, in this case the potential of mean force for both ions increases by less than 0.1 eV as the ions approach the surface. This is caused by the loss of about one water molecule from the first solvation shell.

The total potential experienced by the ions is the sum of the direct interaction with the wire and the potential of mean force caused by the solvent. This potential is always attractive;

therefore both kinds of ions are adsorbed at the surface of the wire without any energy of activation! Since this effect is caused by the geometry of the system, we may conclude that all ions can adsorb at uncharged metallic monoatomic nanowires. Hence, the distinction between non-adsorbing and adsorbing ions, on which much of our understanding of the adsorption behavior on plane electrodes is based, does not hold for monoatomic nanowires.

As an illustration we show a snapshot of a single Na^+ ion adsorbed on the silver wire together with a part of its solvation shell (Figure 3), which we obtain by molecular dynamics.
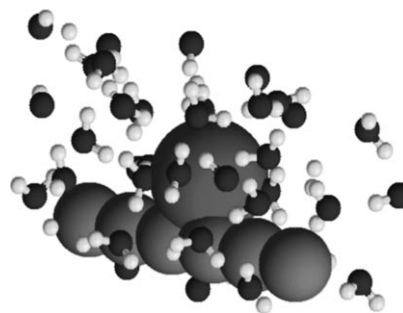
Figure 3. Snapshot a Na^+ ion adsorbed on a Ag wire and some of the surrounding water molecules.

It can be seen that the adsorbed ion is well-solvated. This picture is in striking contrast with the results of ab initio calculations for the adsorption of Na^+ on bulk silver. As was shown by Karttunen and Pakkanen,[18] in this case the stable configuration is an ion fully surrounded by water.

While the preceding calculations show that single ions adsorb, they say little about the behavior of an ensemble, or about the structure of the adsorbate. To explore these questions, we perform molecular dynamics simulations with 35 ions of each kind added to the ensemble. At the end of the simulations all of the ions are adsorbed on the surface of the wire, forming a spiral pattern, in which ions of opposite charge sit next to each other (Figure 4), and the water is displaced from
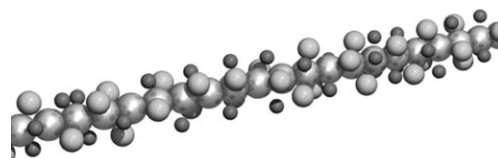
Figure 4. Snapshot of a section of the wire and the adsorbates at the end of the simulations; for clarity, the water is not shown.

the surface. In essence, this structure resembles a one-dimensional salt, in which strands of ions wind around the central wire. The average distance between two choride ions is about 4.5 Å and thus a little larger than in the NaCl crystal (4.1 Å). Due to the small size of the system and the presence of water,

These are not the final page numbers! ↗↗

the structure shows large thermal fluctuations. Further details are given in the Supporting Information.

In the light of the interaction potentials derived above, these adsorbate structures are quite plausible. However, since our molecular dynamics calculations are based on pairwise potentials, we have to check if the inclusion of many-body effects would not alter this effect. We therefore perform DFT calculations, using the VASP code,[24] on a representative sample of our final configuration for the wire and the adsorbate structure without water. The energy needed to remove a pair of Na and Cl atoms is of the order of 1 eV larger than the sum of the single-ion adsorption energies, indicating that the adsorbate structure is stabilized by Coulomb interactions. Using the solution as our reference state (as in Table 1), the energies of desorption are of the order of 6.6 eV. For comparison, the sum of the hydration energies for Na^+ and Cl^- is ca. 7.7 eV. The adsorbed ions are still solvated; of course, the degree of solvation for the adsorbed layer will be less than for a single ion, but even if it were only 1/4 or 1/5, it would still be sufficient to stabilize the adsorbate structure. Thus, the quantum-chemical calculations confirm that the structures resulting from the simulations are real.

Our calculations are performed with a fixed position of the silver atoms, which may induce a certain error. However, relaxation could only lower the energy of the adsorbate structure, and thus enhance the adsorption.

On planar electrodes, a few salt-like adsorbate structures have been observed. Typically, these involve the coadsorption of metals ions with anions. A well-known example is the co-adsorption of Cu and sulphate on Au(111).[23] However, on bulk electrodes these are rare cases, while we expect them to be the rule on wires. Which structures are actually formed on these wires should depend on the type, and particularly the size, of the ions.

It should be possible to verify these results experimentally. In principle, the helical structure can be detected with a scanning tunnelling microscope, though this would be difficult in practice. However, the helical structure should also affect electrochemical measurements as it should only be stable in the vicinity of the potential of zero charge, since a change $\Delta\phi$ in the potential changes the driving force for the adsorption by $ze_0\Delta\phi$, where z is the charge number. Thus, we may expect that the structure breaks down and cations desorb at highly positive potentials, giving rise to a sharp current peak. Also, the adsorption of ions with electronic levels near the Fermi level affects the conductivity, which can be monitored experimentally.[4] The levels of Cl^- lie close to the Fermi level, those of Na^+ not. Thus, the adsorption of the anions can be monitored by the conductivity, and again a change in the anion coverage can be detected.

In summary, we have shown that on monoatomic nanowires the usual distinction between adsorbing and non-adsorbing ions does not hold. All ions are expected to adsorb on these wires, because they lose only a small fraction of their solvation shell in this process. For an aqueous solution of Na^+ and Cl^- in contact with an uncharged silver wire, the adsorbate forms a salt-like structure with spiral patterns.

[1] C. Z. Li, A. Bogozi, W. Huang, J. J. Tao, *Nanotechnology* **1999**, *10*, 221.

[2] H. X. He, S. Boussaad, B. Q. Xu, C. Z. Li, N. J. Tao, *J. Electroanal. Chem.* **2002**, *522*, 167.

[3] C. Shu, C. Z. Li, H. X. He, A. Bogozim, J. S. Bunch, N. J. Tao, *Phys. Rev. Lett.* **2000**, *84*, 5196.

[4] N. J. Tao, C. Z. Li, H. X. He, *J. Electroanal. Chem.* **2000**, *492*, 81; A. Bogozi, O. Lam, H. X. He, C. Z. Li, N. J. Tao, L. A. Nagahara, I. Amlani, R. Tsu, *J. Am. Chem. Soc.* **2001**, *123*, 4585.

[5] E. Leiva, P. Vélez, C. Sanchez, W. Schmickler, *Phys. Rev. B* **2006**, *74*, 035 422.

[6] E. Spohr, *Electrochim. Acta* **2003**, *49*, 23.

[7] S. Izvekov, G. A. Voth, *J. Chem. Phys.* **2001**, *115*, 7196; S. Izvekov, A. Mazzolo, K. Van Opdorp, G. A. Voth, *J. Chem. Phys.* **2001**, *114*, 3248.

[8] A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648.

[9] P. J. Hay, W. R. Wadt, *J. Chem. Phys.* **1985**, *82*, 270.

[10] W. R. Wadt, P. J. Hay, *J. Chem. Phys.* **1985**, *82*, 284.

[11] M. T. M. Koper, R. A. van Santen, *Surf. Sci.* **1999**, *422*, 118.

[12] V. Ranea, A. Michaelides, R. Ramirez, J. Verges, P. Andres, D. King, *Phys. Rev. B* **2004**, *69*, 205 411.

[13] P. Paredes Olivera, A. Ferral, E. Patrito, *J. Phys. Chem. B* **2001**, *105*, 7227.

[14] C. G. Sanchez, *Surf. Sci.* **2003**, *527*, 1.

[15] E. Spohr, G. Tóth, K. Heinzinger, *Electrochim. Acta* **1996**, *41*, 2131.

[16] S. Walbran, A. A. Kornyshev, *J. Chem. Phys.* **2001**, *114*, 10 039.

[17] K. Toukan, A. Rahman, *Phys. Rev. B* **1985**, *31*, 2643.

[18] A. J. Karttunen, T. A. Pakkanen, *J. Phys. Chem. B* **2006**, *110*, 14 379.

[19] I. C. Yeh, M. L. Berkowitz, *Chem. Phys. Lett.* **1999**, *301*, 81.

[20] O. Pecina, W. Schmickler, E. Spohr, *J. Electroanal. Chem.* **1995**, *394*, 29.

[21] H. J. C. Berendsen, J. P. M. Postma, W. F. van Gunsteren, A. DiNola, J. R. Haak, *J. Chem. Phys.* **1984**, *81*, 3684.

[22] C. Hartnig, M. T. M. Koper, *J. Am. Chem. Soc.* **2003**, *125*, 9840.

[23] M. Legault, L. Blum, D. A. Huckaby, *J. Electroanal. Chem.* **1996**, *409*, 79.

[24] G. Kresse, J. Furthmüller, *Phys. Rev. B* **1996**, *54*, 11 169.

↖↖ These are not the final page numbers!
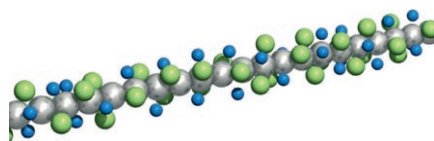
COMMUNICATIONS

Salty strand: Molecular dynamics simulations suggest that a monoatomic silver wire, immersed in an aqueous solution of NaCl, is covered by a monoatomic salt with spiral structure (see picture). This behaviour is in striking contrast to that of a plane silver electrode, on which Na$^+$ does not adsorb. The difference is caused mainly by steric effects.

S. Frank, C. Hartnig, A. Groß,
W. Schmickler*

■■ – ■■

Spiral Adsorbate Structures on Monoatomic Nanowire Electrodes

These are not the final page numbers! ↗↗