Reversible vs. standard hydrogen electrode scale in interfacial electrochemistry from a theoretician's atomistic point of view

Axel Groß*,†,‡

†*Institute of Theoretical Chemistry, Ulm University, 89069 Ulm, Germany*

‡*Helmholtz Institute Ulm (HIU), Electrochemical Energy Storage, 89081 Ulm, Germany*

E-mail: axel.gross@uni-ulm.de

Abstract

It is a general notion in interfacial electrochemistry that the stability of adsorbate phases that only contain hydrogen atoms should be independent of the pH value of the electrolyte on the scale of the reversible hydrogen electrode, whereas the stability of adsorbate phases that do not contain any hydrogen should be independent of the pH value on the scale of the standard hydrogen electrode. In this perspective it will be argued on the basis of a grand-canonical approach that such a Nernstian behavior can only be reproduced if the free energy of the adsorbate phase is independent of the electrochemical control parameters. In general, this should not be true so that the Nernstian behavior should be the exception rather than the rule. Still, structural and chemical factors will be discussed that might lead to a Nernstian behavior. This requires an analysis of the electrochemical electrolyte/electrode interface on the atomistic level. At the same time, this analysis also provides a guideline for the validity of grand-canonical simulations using the concept of the computational hydrogen electrode in which the dependence of the energy of adsorbate phases on pH and electrode potential is neglected.

Introduction

Electrochemical energy storage and conversion is of critical importance for our future sustainable, environmentally friendly energy supply.[1,2] Due to this importance, significant research and development efforts are undertaken worldwide in order to improve our understanding of electrochemical processes at electrolyte/electrode interfaces and to develop more efficient electrochemical devices such as electrocatalysts, fuel cells and batteries. Electrochemistry as a research field can be traced back to the end of 18th century with the experiments of Galvani and Volta.[3] Here I focus on interfacial electrochemistry which is concerned with “structures and processes at the interface between an electronic conductor (the electrode) and an ionic conductor (the electrolyte) or at the interface between two electrolytes”.[3] In particular, I will consider structures at electrochemical electrolyte/electrode interfaces in thermodynamical equilibrium. At such interfaces, usually the existence of an electric double layer (EDL) is proposed based on the assumption that excess charges form on the two sides of the interfaces.[3]

In fact, the concepts to understand the structure of an electric double layer had been developed more than 100 years ago,[4–7] and in principle our understanding of such interfaces is still influenced by these concepts which are based to a large extent on a continuum description of electrochemical interfaces. Although there have been attempts to establish an atomistic view of electrochemistry,[8,9] electrochemistry still appears to be a field whose perception and understanding is based on thermodynamical concepts. These thermodynamical concepts are the consequence of deep insights into the basic rules governing electrochemistry.[3] Still, thermodynamics is a field that deals with measurable macroscopic physical quantities, but a full understanding of the nature of these quantities requires a connection to microscopic properties via statistical mechanics. I will illustrate this using the dependence of adsorbate phases on the pH value and the electrode potential.

In electrochemistry, the concept of potentials is of central importance.[10] For a newcomer in electrochemistry, the subleties between various different potential definitions might cause some confusion. Some potentials depend on position, such as the inner or Galvani potential,[3] some are rather intensive properties such as the electrode potential. Both these potentials are measured in units of a voltage, but for example the electrochemical potential which also is an intensive property is measured in units of an energy.

In this perspective, I will discuss the difference between electrode potentials measured with respect to the standard hydrogen electrode (SHE) and the reversible hydrogen electrode (RHE). In contrast to the SHE, electrode potentials vs. RHE change with the pH value of the electrolyte.[11] As far as equilibrium structures of electrochemical electrolyte/electrode interfaces are concerned, I will particularly address the question what it means if the stability of an interface structure does not change as a function of the electrode potential vs. RHE for different pH values. Admittedly, it appears to me as if there is some confusion about the interpretation of such findings in the literature which baffled me for a long time. Typically it is assumed that hydrogen evolution and oxidation at electrochemical interfaces should follow the Nernst equation. This means that they should be pH-independent on the RHE scale and exhibit a 59 mV shift for every unit of pH change at room temperature on the SHE scale.[12–16] In fact, any deviation from this behavior has been regarded as being "anomalous". Such a Nernstian behavior is well-known from molecular electrochemisty[17] and apparently simply transferred to interfacial electrochemistry. In those cases in which an anomalous behavior has been observed, a broad range of explanations for this phenomenon has been presented. On the one hand, such an anomalous shift has been related to a pH-dependent hydrogen binding energy,[18] but on the other hand, it has been argued that the hydrogen binding energy should be an intrinsic material property and thus not depend on experimental conditions such as the pH value so that other explanations need to be invoked.[16] Conversely, it is assumed that adsorbate phases at electrified interfaces that do not contain any hydrogen should not be pH dependent on the SHE scale.

Here, I will discuss the differences between the SHE and the RHE in interfacial electrochemistry from an atomistic theoretical point of view based on a grand-canonical formalism. I will argue that in principle the stability of any adsorbate structure should be dependent on pH and electrode potential, no matter what specific electrode potential has been chosen. This means that hydrogen equilibrium interface structure should be pH-dependent, even on the RHE scale, and structure not containing any hydrogen should be pH-dependent on the SHE scale. Thus the anomalous behavior should be the rule rather than the exception. Still, I will also give arguments why often these shifts should be rather small.

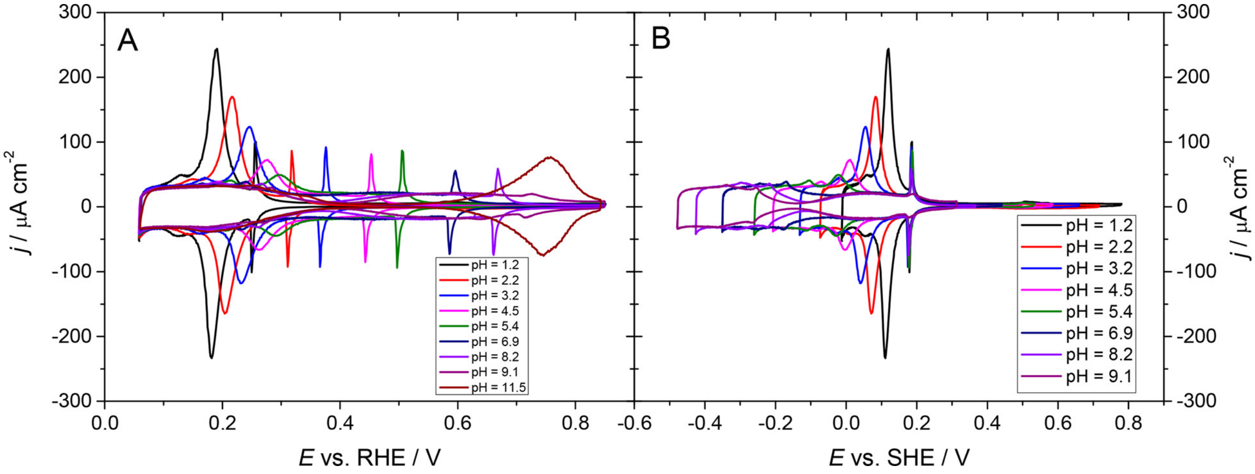

Figure 1: Cyclic voltammograms for Pt(111) in different solutions with pH values ranging from 1.2 to 11.5 in the presence of 10^{-2} M KBr in the RHE scale (A) and in the SHE scale (B). (Reprinted with permission from Ref.[19] Copyright 2018 American Chemical Society.)

Motivation

The study of processes at electrochemical interfaces involving hydrogen adsorption and desorption is of considerable interest, both from a fundamental as well as from a technological point of view due to its importance in electrochemical energy conversion. In fact, whenever aqueous electrolytes are involved, then naturally hydrogen adsorption can occur due to the fact that there is always a non-zero concentration of protons in the electrolyte. As an illustration of such a study, I have picked a recent experimental study of bromide adsorption on Pt(111)[19] which had also been studied theoretically by first-princples calculations.[20,21] At electrochemical interfaces between an aqueous electrolyte and in particular metal electrodes, at low electrode potentials at which the electrode is more negatively charged, cation adsorption is more favorable (here proton adsorption), whereas at higher potentials at which the electrode is more positively charged, anions such as halides adsorb preferentially. In fact, experimentally a competitive adsorption of hydrogen and halides on Pt(111) has been observed at low pH values,[22,23] i.e., upon increasing the electrode potential adsorbed hydrogen is replaced by chloride or bromide, respectively, which has also been confirmed in first-principles calculations.[20,21]

Figure 1 shows cyclic voltammograms of Pt(111) in the presence of 10^{-2} M KBr for different pH values both on the RHE (panel A) and the SHE (panel B) scale. First of all it can be seen that the voltammograms are rather symmetric indicating that the peaks correspond to reversible processes. There are two prominent peaks in each scan. First, there is large broad peak at 0.18 V vs RHE at pH = 1.2 which shifts to higher voltages for increasing pH values and splits to a certain extent. This peak is associated with hydrogen adsorption/desorption and bromide adsorption/desorption [19] which strongly overlap at low potentials indicating the competitive nature of hydrogen and bromide adsorption.[23] Whereas this peak shifts to higher voltages with increasing pH vs RHE, it shifts to lower voltages vs SHE, thus showing a non-Nernstian behavior. There is another sharp peak at 0.2 V vs. SHE which stays constant on the SHE scale as a function of pH. It is attributed to a Pt(111)(4×4)-7Br to Pt(111)(3×3)-4Br transition which does not involve any hydrogen and therefore should be pH independent on the SHE scale.[19]

Theoretical methodology

As discussed in the previous section, the peaks in the cyclic voltammograms shown in Fig. 1 are associated with reversible changes in the structure and coverage of the electrode surface. The stable equilibrium structures of electrochemical electrolyte/electrode interfaces can be conveniently determined using grand-canonical schemes as a function of the electrochemical environment.[24,25] This environment is characterized by the electrode potential U and the activities a_i of the species i solvated in the electrolyte which for an ideal solution corresponds to their concentration or for protons can be expressed through the pH value. In order to determine the stable structures, it is helpful to subdivide the electrolyte/electrode interface into three regions as illustrated in the lower part of Fig. 2: bulk electrode, bulk electrolyte and the interface region. Furthermore, we assume that there is thermal equilibrium throughout the system which means that the (electro-)chemical potentials of the species present in the

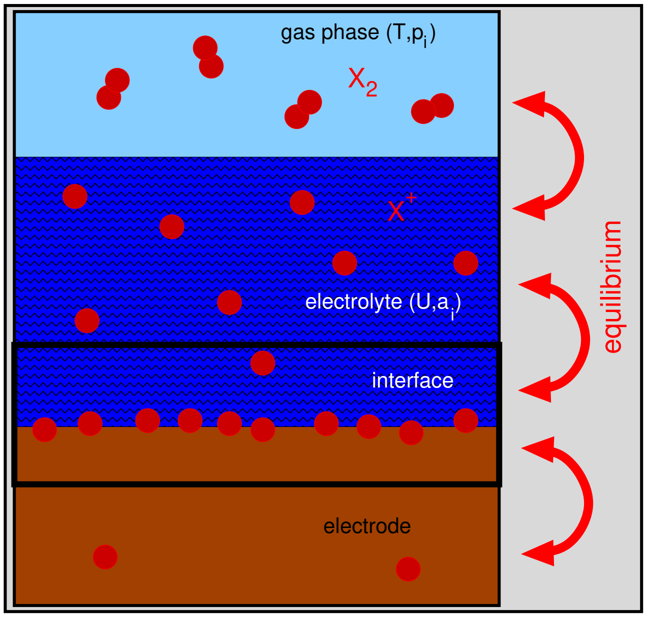

Figure 2: Illustration of a grand-canonical scheme to determine the equilibrium structure of electrode-electrolyte interfaces. The inclusion of the gas phase is the basis for the concept of the computational hydrogen electrode (CHE).[24,26] The interface region is given by the area in the box (adapted from Ref.[25]).

systems are constant throughout the whole system.

Now consider a clean interface without any adsorbates. A species i present in the electrolyte will adsorb at the electrochemical interface if the free energy difference

$$\Delta G^{ads}(T,U,a_i,N_i) \ = G^{\text{interf}}(T,U,a_i,N_i) - G^{\text{interf}}(T,U,a_i,0) - N_i \ \tilde{\mu}_i(T,U,a_i) \qquad (1)$$

for the adsorption of N$_i$ particles of species i in the interface region is negative. $G^{\text{interf}}(T,U,a_i,N_i)$ is the free energy of the interface region with N_i adsorbates of species i present in the interface region and $\tilde{\mu}_i(T,U,a_i)$ the electrochemical potential of species i. Now it is important to realize that it is not the free energy of adsorption per particle of species i that determines the thermodynamically stable interface structure but rather the free energy of adsorption per surface area A_S:[25]

$$\Delta\gamma(T,U,a_i,N_i) = \Delta G^{ads}(T,U,a_i,N_i)/A_S \qquad (2)$$

From now on we implicitly assume that we have a periodic adsorbate structure and that A_S is the surface area of the unit cell with N_i adsorbed species.

One critical problem in calculating the adsorption free energy ΔG^{ads} according to Eq. 1 is due to the fact that the determination of the electrochemical potential $\tilde{\mu}_i(T, U, a_i)$ typically requires the evaluation of solvation energies which is computationally rather demanding.[27] However, this evaluation can be avoided by relating the electrochemical potential of the solvated species to the chemical potential of corresponding gas-phase species via the redox potential which is the basis of the concept of the computational hydrogen electrode (CHE) proposed by Nørskov *et al.*[24,26] For hydrogen adsorption this means that the electrochemical potential of hydrogen can be expressed as

$$\tilde{\mu}_{\mathrm{H}} = \tilde{\mu}_{\mathrm{H^+(aq)}} + \tilde{\mu}_{e^-} = \frac{1}{2}\mu_{\mathrm{H_2(g)}} - eU_{\mathrm{SHE}} - k_{\mathrm{B}}T\ln(10)\mathrm{pH} = \frac{1}{2}\mu_{\mathrm{H_2(g)}} - eU_{\mathrm{RHE}}\ . \tag{3}$$

This equation requires some clarification. First of all I have written the electrochemical potential of hydrogen as the sum of the electrochemical potentials of the proton and the electron. Note that in Eq. 1 the energy for the adsorption of N_i particles of species i is considered. Note furthermore that in thermal equilibrium electrochemical electrolyte/electrode interface have to be overall charge neutral because otherwise there would be a net electric field which would attract or repel charge particles with respect to the interface.[28] So the presence of a proton close to the interface requires the presence of a corresponding countercharge which usually means for metallic electrodes that there is an additional electron at the Fermi level in the electrode. Hence the adsorption of a proton at this electrified interface leads effectively to the adsorption of a hydrogen atom on the electrode, and therefore we have to take the electrochemical potential $\tilde{\mu}_{\mathrm{H^+(aq)}} + \tilde{\mu}_{e^-}$ of a solvated hydrogen atom as a reference.

Furthermore, Eq. 3 also demonstrates that it does not matter whether the electrode potential is given on the SHE or the RHE scale (or any other potential scale), the electrochemical potential has to be independent of the choice of the reference for the electrode potential. Hence the CHE is neither a “RHE concept” nor a “SHE concept”, it is just a grand-canonical concept. Consequently, also the adsorption energy cannot not depend on the particular choice of the electrode potential scale. Hence the free energy of hydrogen adsorption per surface area at electrochemical interfaces as a function of the electrochemical control parameters can for example be expressed as

$$\Delta\gamma_{\mathrm{H}}(T,U,\mathrm{pH},N_{\mathrm{H}}) = \frac{N_{\mathrm{H}}}{A_S}\left(\Delta G_{\mathrm{H}}^{ads}(T,U,\mathrm{pH}) + eU_{\mathrm{SHE}} + k_{\mathrm{B}}T\ln(10)\mathrm{pH}\right) \tag{4}$$

where

$$\Delta G_{\mathrm{H}}^{ads}(T,U,\mathrm{pH}) = \frac{1}{N_{\mathrm{H}}}\left(G_{A_S}^{\mathrm{interf}}(T,U,\mathrm{pH},N_{\mathrm{H}}) - G_{A_S}^{\mathrm{interf}}(T,U,\mathrm{pH},0)\right) - \frac{1}{2}\mu_{\mathrm{H_2(g)}} \tag{5}$$

corresponds to the free adsorption energy per hydrogen atom in the structure with N_{H} adsorbed hydrogen atoms per surface area A_S with respect to the hydrogen molecule in the gas phase. This concept can also be used for the adsorption of, e.g., halides A^- with A = F, Cl, Br, I, where typically the redox couple is given by $\frac{1}{2}$ $\mathrm{A}_2 + e^- \rightleftarrows \mathrm{A}^-$ yielding an electrochemical potential of[29,30]

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

where U^0 is the reduction potential of the halide vs. U_{SHE} and a_{A^-} its activity coefficient. Furthermore, also any mixed adsorbate phase can be addressed using this approach.

Discussion

In the previous section, I described the grand-canonical approach to determine the thermodynamically stable adsorbate phases at electrochemical electrolyte/electrode interfaces. In order to avoid the evaluation of solvation energies of solvated species, the concept of the computational hydrogen elecrode[24,26] has been employed. It is important to note that up to here all expressions are exact, as far as the description of structures in thermodynamic equilibrium is concerned. However, the evaluation of the corresponding expressions requires the determination of free energies which is typically numerically rather demanding as it necessitates performing, e.g., thermodynamic integration schemes.

Hence typically in the application of the CHE, the free energy difference appearing in Eq. 5 is replaced according to

$$G_{A_S}^{\mathrm{interf}}(T, U, \mathrm{pH}, N_{\mathrm{H}}) - G_{A_S}^{\mathrm{interf}}(T, U, \mathrm{pH}, 0) \;\approx\; E_{A_S}^{\mathrm{interf}}(N_{\mathrm{H}}) - E_{A_S}^{\mathrm{interf}}(0) \tag{7}$$

which means that the difference in the free energies is replaced by the difference in total energies, and in the evaluation of the total energies the electrochemical control parameters are neglected, i.e., the interface energies are assumed to be independent of the electrode potential and proton concentration. Often the electrochemical environment is entirely neglected, i.e., the total energies are calculated at the vacuum/electrode interface instead of the electrolyte/electrode interface.[20,30] Still it is important to emphasize that this is not an approximation that is inherent to the CHE, as is often assumed, but rather a typical approximation applied when employing the in principle exact concept of the CHE.[25]

I will now discuss a typical example presented in Fig. 3 where the approximations just mentioned have all been invoked. This figure displays a Pourbaix diagram, i.e., a phase diagram as a function of pH and the electrode potential, calculated within the concept of the CHE .[21] This Pourbaix diagram addresses exactly the same system as covered in Fig. 1, namely the co-adsorption of hydrogen and bromide on Pt(111) in the presence of an aqueous electrolyte. In these calculations, a fixed bromide concentration corresponding to an activity of $a = 0.1$ has been assumed that might be somewhat larger than the concentration of 10^{-2} M KBr used in the experiments .[19]

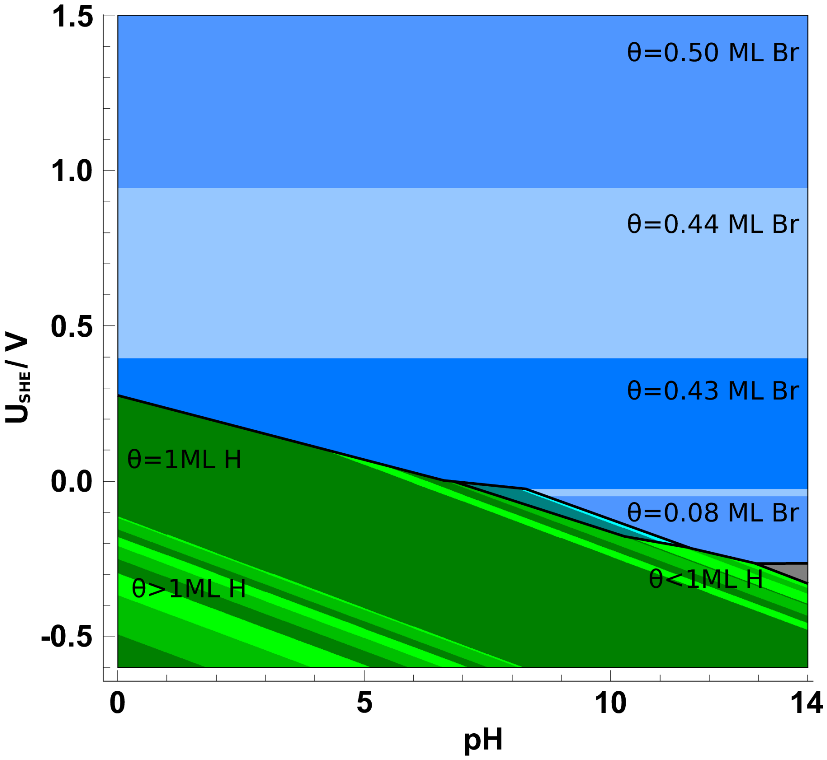

Figure 3: Calculated Pourbaix diagram, i.e., a map of the stable phases of co-adsorbed bromine and hydrogen on Pt(111) as a function of pH and electrode potential for a fixed bromide concentration corresponding to an activity of $a = 0.1$. Greenish colors denote a pure hydrogen phase, bluish colors a pure bromine phase. In between the hydrogen and bromine phases, there is a thin region, where a co-adsorbate structure with both species is stable. The gray area corresponds to a region where the clean, uncovered electrode is stable. (Reprinted with permission from Ref.[21] Copyright 2016 American Chemical Society.)

The greenish phases in Fig. 3 correspond to pure hydrogen adsorbate phases, the bluish ones to pure bromide adsorbate phases. Furthermore, there is a small pocket of mixed hydrogen-bromide adsorption phases at intermediate pH values. However, at low pH values, the DFT calculations nicely reproduce the competitive adsorption of hydrogen and bromide observed in the experiment,[19,23] i.e., the adsorbed hydrogen is replaced by adsorbed bromide upon increasing the electrode potential.

Replacing the free energies in Eq. 5 by total energies according to Eq. 7 means that the dependence of the stability of the pure hydrogen adsorbate phase on pH only enters through the term $k_{\mathrm{B}}T\ln(10)\mathrm{pH}$ appearing in the electrochemical potential of the solvated protons. Also the electrode potential does not affect the difference in the interface energies. And sure enough, the boundaries between the pure hydrogen adsorption phases all exhibit a slope of 59 mV/pH, i.e., they exhibit a perfect Nernstian behavior. Now this Nernstian behavior has not been observed in the experiment.[19] This descrepancy between the experiment and theory can thus only be caused by the replacement of the free adsorption energy with respect to the H_2 molecule in the gas phase by the corresponding total adsorption energy. Hence, the non-Nernstian behavior can only be due to the pH and U dependence of the free energy difference $\Delta G_{\mathrm{H}}^{ads}(T, U, \mathrm{pH})$ expressed in Eq. 5.

Indeed, note that a change in the pH value and in the electrode potential U will modify the structure of the electric double layer (EDL) at the electrolyte/electrode interface which will alter the local electric fields and cause a charge rearrangement at the surface.[28] Furthermore, it is rather unlikely that a change in pH and in U_{SHE} that would leave the electrochemical potential of the protons constant, i.e., that would keep the electrode potential vs RHE constant, should cancel in the free energy difference $\Delta G_{\mathrm{H}}^{ads}(T, U, \mathrm{pH})$, as a change in the proton concentration and the electrode potential correspond to two different physicochemical processes. Thus there is no reason to believe that a change of the pH on the RHE scale should not change the free adsorption energy and thus lead to a non-Nernstian behavior. Therefore it should be the rule rather than the exception that hydrogen equilibrium interface structures should be pH-dependent on the RHE scale.

Another interesting feature of the cyclic voltammograms shown in Fig. 1 is the observation that the peak related to the change in the bromide structure does not depend on the electrode potential on the SHE scale. Interestingly enough, in the calculations presented in Fig. 3, also a structural change in the bromide adlayer from a $(\sqrt{7} \times \sqrt{7}R19.1^\circ)$-3Br to a (3×3)-4Br structure has been found. This is not exactly the same transition as the one attributed to the corresponding peak by Mello *et al.*[19] where a (4×4)-7Br has been assumed at lower electrode potentials, however, the coverage change upon this transition is almost the same. It is also gratifying to see that the calculations at least qualitatively reproduce the experimental observation[19] that towards alkaline conditions the bromide adsorption peak separates from the hydrogen desorption peak. Note however, that OH adsorption is not considered in the calculations which might replace bromide adsorption in very alkaline conditions.[19]

With respect to the fact that this transition between two different bromide adsorption phases is pH independent, both theory and experiment thus agree. But again, there is no fundamental reason to presuppose that the free energy difference $\Delta G_{\mathrm{H}}^{ads}(T, U, \mathrm{pH})$ with regard to bromide adsorption should be independent of any changes in pH. However, there are good arguements why this free adsorption energy in particular of small ions such as protons or halides at electrochemical interfaces between an aqueous electrolyte and a metal electrode should be rather independent of pH and electrode potential. Note that at $\mathrm{pH} = 0$, there is one proton per 55 water molecules. Already at $\mathrm{pH} = 2$, there are 5500 water molecules per one proton. Although the proton concentration close to the electrochemical interface might be larger than in the bulk electrolyte, it is rather unlikely that such a minute concentration of protons should change the hydrogen adsorption energies. Furthermore, electric field effects directly at metal electrodes are very effectively shielded due to the fact that an electric field cannot penetrate into an ideal conductor.[31] This provides an explanation why changes in the electrode potential might hardly affect the adsorption energies of small atomic adsorbates such as hydrogen and halides. And last but not least, even the presence of water hardly modifies adsorption energies of atoms at metal surfaces due to the relatively weak interaction of water with metal surfaces and the comparable large distance of the water molecules from the surface.[24,32,33]

One can now turn the argumentation around with respect to the validity of the approximations often entering applications of the concept of the computational hydrogen electrode. Recent theoretical studies have correctly emphasized that it is important to take the electrochemical environment adequately into account in the modelling of electrolyte/electrode interfaces.[34–37] However, for those electrochemial interfacial systems in which hydrogen adsorbate phases exhibit a Nernstian behavior or in which the stability of non-hydrogen adsorption phases does not depend on pH, it can in principle safely be assumed that the free energy difference $\Delta G_{\mathrm{H}}^{ads}(T, U, \mathrm{pH})$ does not depend on the electrochemical control parameters, so that this difference can be replaced by the difference in the respective total energies. This also provides an explanation why the typical approximation applied when doing calculations of electrochemical interfaces using the concept of the computational hydrogen electrode,[28,38–43] namely to neglect the influence of electrode potential and pH when calculating the energy of the adsorbate phases, has often yielded results that agree rather nicely with the experiment.

To wrap up this discussion of the difference between the reversible and the standard hydrogen electrode, I will present another example of a Pourbaix diagram produced using the concept of the CHE neglecting the pH and electrode potential dependence in the adsorption energy with respect to the free H_2 molecule. This example is concerned with the adsorption of sulfate and hydrogen on Pt(111) and Au(111).[38] Note that similar results for Au(111) as presented in Ref.[38] have also been found in a recent joint experimental-theoretical work.[44] Here, however, I will concentrate on sulfate adsorption on Pt(111). On this surface, sulfate adsorbs at potentials of about 0.5 V in a row-like $\sqrt{3} \times \sqrt{7}$ structure[45] whereas the corresponding structure appears on Au(111) at potentials of about 1 V.[46] Still, DFT calculations neglecting the explicit presence of water molecules on these surfaces fail to reproduce the prensence of any stable row-like sulfate structures at the experimentally observed conditions.[38] Also the inclusion of water within an implicit solvent model[47] could not heal this discrepancy between experiment and theory.

However, using a combination of the implicit solvent model with explicitly considered water molecules, a very satisfactory agreement with the experiment has been obtained. This is demonstrated in Fig. 4 where a Pourbaix diagram for the co-adsorption of sulfate and hydrogen on Pt(111) is shown. At low electrode potentials, Pt(111) is hydrogen-covered, and at about 0.4 V the so-called double layer region starts, in which Pt(111) is not covered by any adsorbate, followed by the onset of sulfate adsorption. The structure of the stable row-like $\sqrt{3} \times \sqrt{7}$ sulfate phase is illustrated in the inset of Fig. 4. This sulfate row-like structure becomes strongly stabilized by the presence of two explicit water molecules per

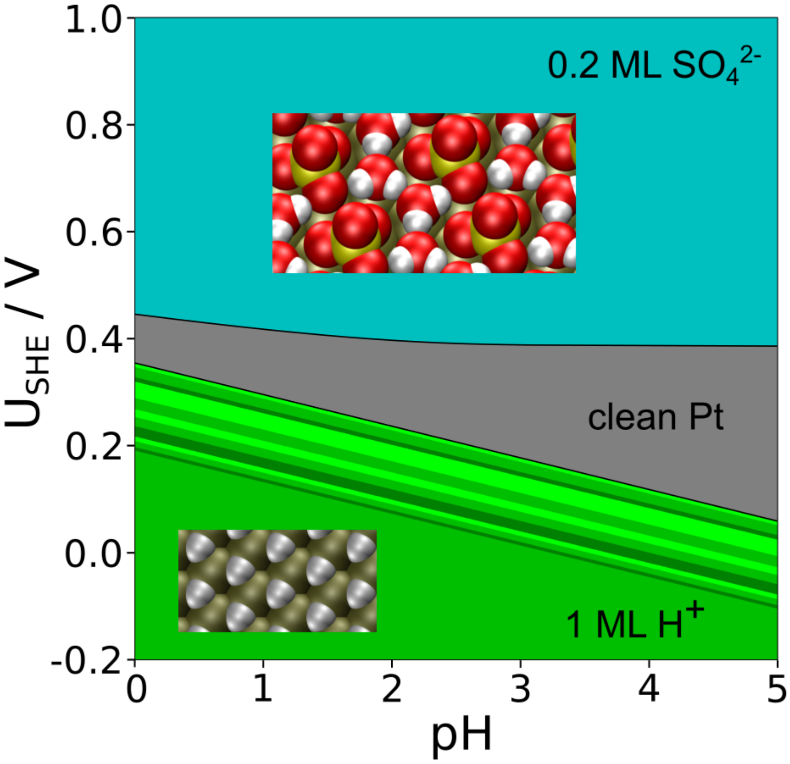

Figure 4: Calculated Pourbaix diagram showing the stable phases of co-adsorbed sulfate and hydrogen on Pt(111) as a function of pH and electrode potential .[38] The sulfate concentration corresponds to an activity of 0.1. (Reprinted with permission from Ref.[25] Copyright 2021 Elsevier.)

sulfate anion linking the sulfate rows. These water molecules are strongly bound with a binding energy that is much higher than the water cohesive energy[38,44] so that they become an integral immobile element of the sulfate adsorbate structure.

This example shows that the presence of water can indeed have a significant influence on the stability of adsorbate phases at interfaces between aqueous electrolytes and electrodes, even without the explicit consideration of pH and the electrode potential. However, in the case of sulfate adsorption on Pt(111) and Au(111) the combination of frozen water rows together with an implicit solvent was sufficient to yield a qualitative and semi-quantitative agreement with experiment.[38,44] In general, the liquid nature of water has to be appropriately taken into account in order to faithfully model water/electrode interfaces. Unfortunately, considering the explicit presence of water molecules requires to perform time-consuming averages, for example based on *ab initio* molecular dynamics (AIMD) simulations.[48–51] As an computationally attractive alternative, the explicit description of water molecules might be replaced by using implicit solvent models in which the solvent is described by a dielectric continuum just characterized by its dielectric constant.[35,36] Unfortunately, benchmark calculations found substantial deviations between AIMD and implicit solvent approaches,[52] as far as the influence of solvation on adsorption energies is concerned. Hence it appears fair to say that further work is required to obtain a reliable and at the same time computationally attractive approach to model interfaces between aqueous electrolytes and electrodes.

Note that the calculations presented in Fig. 4 also reproduce the experimentally observed displacement of sulfate adsorption to higher potentials for decreasing pH, in particular for pH≥2,[53] resulting in a curved phase boundary between clean Pt and the sulfate adsorption phase. This is interesting as the pH value does not directly enter the electrochemical potential of sulfate[38] under equilibrium conditions. However, there is an acid/base equilibrium between protons, sulfate and bisulfate anions $HSO_4^- \rightleftharpoons SO_4^{2-} + H^+$. Furthermore, for the calculation of the Pourbaix diagrams, the total concentration of anions c_i in the electrolyte has to be kept fixed which makes the molar fraction x_i of SO_4^{2-} pH-dependent according to[38]

$$x_{SO_4^{2-}} = \frac{1}{1 + 10^{-pH}/10^{-pK_a}} \,. \tag{8}$$

Thus it is the molar fraction of sulfate through through which the onset of the sulfate adsorption phase becomes pH-dependent.

It is important to recall that the two Pourbaix diagrams just discussed were determined using the approximation that the adsorption energies of the considered adsorbate phases do not depend on electrode potential and proton concentration. Thus the dependence of the stable phases on electrode potential and pH entirely stems from the corresponding dependence of the electrochemical potential of the species in solution. And as already discussed above, this is exactly the assumption the Nernstian view on the stability of adsorbate phases is based on, as it only takes the thermodynamics of the bulk electrolyte into account. This is also the reason why these calculations yield a stability of pure hydrogen adsorbate phases that changes by 59 mV/pH whereas the stability of adsorbate phases that contain no hydrogen are indendent of pH. The sulfate example shown in Fig. 4 demonstrates that only adsorbate phases that involve species consisting of hydrogen and other elements can exhibit a non-trivial dependence on electrode potential an pH. This is in fact also illustrated for the small pocket of mixed H-Br adsorbate phases in Fig. 3. Overall, this means that those interfacial systems for which grand-canonical simulations employing the approximation Eq. 7 are able to faithfully reproduce the experimentally observed existence of stable adsorbate phases are dominated by a Nernstian behavior, i.e., the dependence of the stable adsorbate phases on the electrochemical control parameters pH and electrode potential, are governed by the properties of the bulk electrolyte. And any deviation from this behavior requires a careful analysis of the stability determining factors of the explicit adsorbate phases on an atomistic level.

Conclusions

In this perspective, the stability of adsorbate phases at electrochemical electrolyte/electrode interfaces has been addressed from a theoretical atomistic point of view based on a grand-canonical approach. As for any adsorbate phase, its thermodynamic stability is governed both by the reservoir the adsorbate orginates from and by the free energy of the adsorbate structure. Neglecting the dependence of the free energy of the adsorbate structure on pH and electrode potential leads to a Nernstian behavior, i.e., the stability of adsorbate phases that only contain hydrogen atoms becomes independent of the pH value of the electrolyte on the scale of the reversible hydrogen electrode, whereas the stability of adsorbate phases that do not contain any hydrogen becomes independent of the pH value on the scale of the standard hydrogen electrode. Indeed, there are good arguements on the atomistic level, in particular for the case of small atomic adsorbates on metal electrodes, which make these assumptions underlying the Nernstian behavior reasonable. These arguements also explain the success of grand-canonical simulations of adsorbate phases using the concept of the computational hydrogen electrode in which the influence of the electrochemical control parameters on the energy of the adsorbate phases are neglected. In general, however, this approximation should not be valid. Changing electrode potential and/or pH alters the structure of the electric double layer at the interface which will also modify the local electric field close to the electrode. Hence there is no reason to assume that the free energy of electrified interfaces should be independent of electrode potential and pH. Therefore the "normal" Nernstian behavior should be the exception rather than the rule. Consequently, the study of any adsorbate structure at electrochemical interfaces requires a careful analysis of the factors influencing its stability on the atomistic level.

Biography

Axel Groß obtained his Diploma in Physics from the University of Göttingen in 1990 and his Ph.D. 1993 in Theoretical Physics at the Technical University of Munich. After five years as a staff scientist in the Theory Department of the Fritz-Haber-Institute of the Max-Planck-Society in Berlin, he became Associate Professor in Theoretical Physics/Surface

Physics at the Technical University of Munich. In 2004 he was appointed as a Full Professor in Theoretical Chemistry at Ulm University; furthermore, in 2011 he became PI at Helmholtz Institute Ulm (HIU) Electrochemical Energy Storage. His research interests focus on the first-principles modelling of atomistic structures and processes at surfaces and at solid–gas and electrochemical electrode–electrolyte interfaces in electrochemical energy conversion and storage, reactions in heterogeneous and electro-catalysis, and materials modelling related to properties of batteries.

Declaration of interests

none

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