

Modelling the electric double layer at electrode-electrolyte interfaces

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Abstract

The description of electrode-electrolyte interfaces is based on the notion of the formation of an electric double layer. Most of the concepts underlying its structure and properties have been developed more than one hundred years ago based on continuum approaches. Still, a complete atomistic theoretical description is missing. Here first the traditional models of the electric double layer will be briefly reviewed before recent atomistic approaches will be presented. Finally, the importance of the formation of an electric double layer at electrode-electrolyte interfaces in batteries will be discussed.

Keywords: Electric double layer, electrochemical interfaces, electrochemical modelling, first-principles simulations, Pourbaix diagram, batteries

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I. INTRODUCTION

Recently there has been considerable progress in the theoretical description of electrocatalytic reactions from first principles (see, e.g., [1–5]). However, still the modelling of electrocatalytic reactions is hampered by two factors. First, the crucial control parameter for electrochemical processes is the electrode potential, but its proper consideration in electronic structure calculations is not easy. In principle, it requires to use a grand-canonical treatment with respect to the number of electrons which also means that one has to deal with charged systems [6–8]. Second, electrocatalytic reactions occur at the interface between an electrode and an electrolyte where an electric double layer (EDL) forms. This means that the proper concentration of ions at the interface needs to be considered [9, 10]. Furthermore, in the case of liquid electrolytes the statistical nature of the liquid needs to be taken into account which means that the proper statistical averages have to be performed [11]. And it is fair to say that most of the first-principles studies for electrocatalytic reactions ignore the presence of an EDL or model it in a very approximate way.

Here we will briefly review current theoretical attempts to properly describe aspects of the double layer that are crucial for processes in electrochemical energy conversion and storage. First we will outline the basic continuum concepts underlying the description of the electric double layer. Then we will address recent attempts to model the electric double layer atomistically based on first-principles simulations. Furthermore, we will show how the equilibrium coverage of electrodes with ions can be determined in a grand-canonical approach. Finally we will elucidate that the formation of electric double layers at electrode/electrolyte interfaces is also crucial for devices in electrochemical energy storage.

II. CONTINUUM AND ATOMISTIC DESCRIPTION OF THE ELECTRIC DOUBLE LAYER

The concepts to understand the structure of an electric double layer have been developed more than 100 years ago [12–15]. Helmholtz is given credit for being the first to realize that a charged electrode will attract counterions from the electrolyte [16], as illustrated in Fig. 1a. This leads to a linear potential drop within this *Helmholtz layer*. Effectively, two layers of opposite polarity form at the interface between electrode and electrolyte, resulting

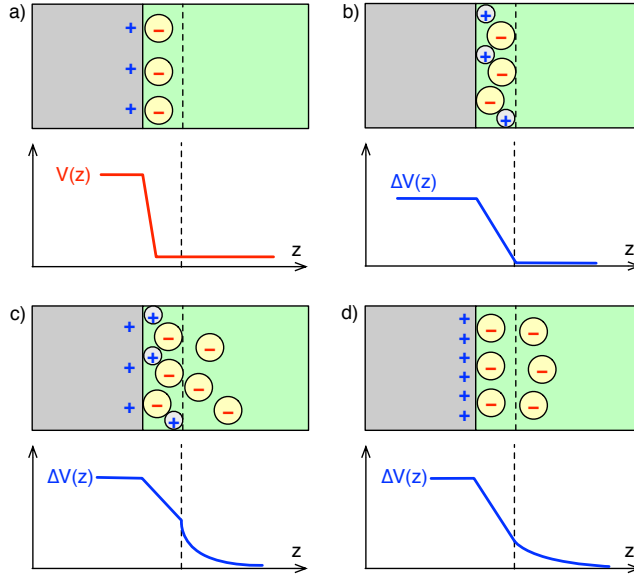


FIG. 1. Illustration of possible scenarios for electric double layers. a) Charged electrode covered by counter ions; b) two layers of oppositely charged ions at uncharged electrode; c, d) scenarios depicted in panel a and b, respectively, with an additional diffuse layer of ions.

in a capacitor. A similar linear potential drop can also be caused by two layers of oppositely charged ions at the electrode (see Fig. 1b).

The Helmholtz model was refined by Gouy [13] and Chapman [14] by assuming a diffuse thermal distribution of the ions. Applying Boltzmann statistics to the distribution of both anions and cations of absolute charge $|ze|$ with a bulk density of n_0 [17], the *Poisson-Boltzmann equation* for the potential $V(x)$ can be derived, which for small charge densities at the electrode leads to an exponentially decreasing electric potential.

However, for high electrolyte concentrations, the Gouy-Chapman theory shows characteristic deviations from experimental observations. Stern therefore suggested to use a combination of the Helmholtz and Gouy-Chapman models for an improved description of the double layer [15]. This leads to a combination of linearly and exponentially decreasing potentials with the double layer region, as illustrated in Figs. 1c and d. At high electrolyte concentrations, the Helmholtz layer gives the dominating contribution to the overall capacitance. Note that this continuum formulation of the EDL at the interface between an electron conductor (the electrode) and an ion conductor (the electrolyte) is rather close to the macroscopic treatment of the interface between an electron conducting n-type and a

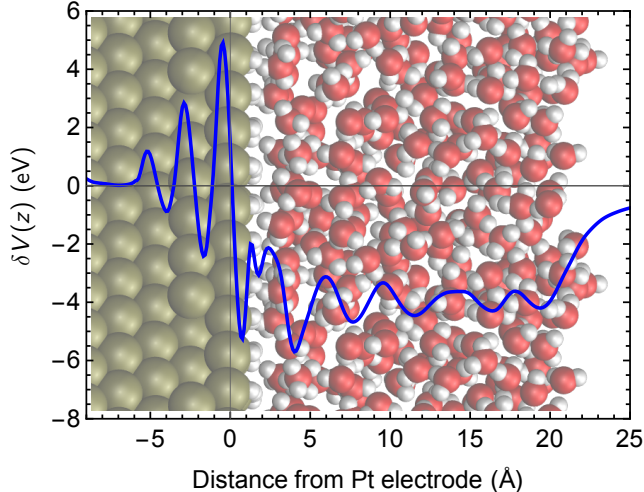


FIG. 2. Difference $\delta V(z)$ of the electrostatic potential of Pt(111) in vacuum and of hydrogen-covered Pt(111) with a water film averaged over a 40 ps AIMD run together with a snapshot of the AIMD trajectory with six layers of water on the hydrogen-covered Pt(111) electrode [23].

hole conducting p-type semiconductor.

The Stern model still has limitations. The electrode is considered to be a perfect conductor, ions are treated as point charges, and all interactions are assumed to be of electrostatic nature. There have been numerous attempts to improve the description [17–19], but most of these approaches have still been on a continuum level. Recently, there have been increased efforts to understand the structure of electrode/electrolyte interfaces from an atomic level, mainly using *ab initio* molecular dynamics simulations based on periodic density functional theory calculations [11, 20–22]. These simulations have concentrated on metal electrode/water interfaces. A snapshot of a AIMD simulation together with the averaged potential dependence is shown in Fig. 2 [23]. The difference $\delta V(z)$ of the electrostatic potential of Pt(111) in vacuum and of hydrogen-covered Pt(111) with a water film is plotted so that the change of the electrostatic potential within the Pt electrode upon the interaction with the aqueous electrolyte becomes apparent.

There are several distinct differences with respect to the schematic scenarios for the EDL shown in Fig. 1. First of all, the presence of the aqueous electrolyte together with the hydrogen layer causes a significant charge rearrangement within the first three layers of the Pt electrode. Second, within the layer of adsorbed protons the potential first drops, but then it increases again. And third, the layered structure of the electrolyte close to the electrode

introduces an oscillatory dependence of the potential as a function of the distance from the electrode. Note that a detailed analysis of the charge rearrangement given by electronic structure calculations shows that there is a significant polarization of the water molecules close to the electrode [7, 23], but also larger ions adsorbed on metal electrodes can become strongly polarized [24].

Such AIMD simulations provide valuable insights into the atomic and electronic structure of an EDL. Still the underlying first-principles calculations are computationally rather demanding. Because of the limited number of such studies, at the moment there are no systematic trends derived from first-principles simulations with respect to the potential dependence within the EDL. Thus there is certainly a need for further AIMD studies addressing the structure of the EDL for various electrode/electrolyte combinations.

Furthermore, an important input into the AIMD simulation is the equilibrium ion coverage of the electrode which cannot be derived from the AIMD simulations. This is important as for example the formation of a layer of specifically adsorbed anions can dramatically influence the electrocatalytic properties of an electrode [10, 25]. In the next section, we will discuss how this equilibrium coverage can be rather elegantly derived from first-principles calculations incorporating the electrochemical environment in a grand-canonical approach.

III. EQUILIBRIUM COVERAGE OF METAL ELECTRODES

In the preceding section we have seen that the concentration of ions on the electrode surface can be decisive for the extent of the electric double layer and the size of the potential drop across the electric double layer. Hence it is important to derive the equilibrium ion coverage of the electrode as a function of electrode potential and ion concentration in the electrolyte.

This seems to be a complicated task, but in fact it can be done relatively easily based on the concept of the computational hydrogen electrode (CHE) [1, 26]. Let us first start with the proton coverage as any aqueous electrolyte contains a certain concentration of protons given by the pH value.

In order to calculate the adsorption energy of any ion on an electrode, the energy of the reference state in the electrolyte, the electrochemical potential $\tilde{\mu}$ of the solvated ion, needs to be known. The calculation of solvation energies can be quite cumbersome as it

in principle requires thermodynamic integration schemes. Yet, the calculations of solvation energies can be avoided by realizing that most ions can be related to a corresponding gas phase species through their standard electrode potential. This is the basis of the concept of the computational hydrogen electrode. For example, the electrochemical potential of protons in an aqueous solution is given by [26]

$$\tilde{\mu}_{\text{H}^+(\text{aq})} + \tilde{\mu}_{e^-} = \frac{1}{2}\mu_{\text{H}_2(\text{g})} - eU_{\text{SHE}} - k_{\text{B}}T \ln(10)\text{pH}, \quad (1)$$

where one has used the fact that at standard conditions defining the standard hydrogen electrode potential U_{SHE} the solvated proton is in equilibrium with the H_2 molecule in the gas phase.

This concept is not only applicable for hydrogen and protons, it works also for any redox couple such as $\frac{1}{2} \text{A}_2 + e^- \rightleftharpoons \text{A}^-$ [27, 28] where A_2 can be for example a halogen molecule, resulting in an electrochemical potential

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

where U^0 is the reduction potential of the corresponding halide vs. U_{SHE} and a_{A^-} its activity coefficient. This concept can also be extended to more than one solvated species in the electrolyte [29].

In order to determine the equilibrium adsorption structure, the free energy of adsorption

$$\Delta\gamma = \frac{1}{A_{\text{S}}}\left(G_{\text{ads}} - \sum_i n_i \Delta\tilde{\mu}_i(T, a_i, U)\right). \quad (3)$$

has to be evaluated [29], where G_{ads} is the free energy of adsorption and $\Delta\tilde{\mu}_i(T, c_i, U)$ is the contribution to the electrochemical potential that depends on temperature, concentrations c_i and electrode potential that can be derived using the expressions given in Eqs. 1 and 2.

Up to here everything is exact. However, the determination of the free energy of adsorption G_{ads} is often rather cumbersome. Therefore, often entropic effects and the presence of the electrochemical environment are neglected [26] which means that G_{ads} is replaced by the total energy of adsorption E_{ads} at the electrode-vacuum interface.

Hence the whole dependence on the particular electrochemical conditions is only taken into account with respect to the solvated species in the electrolyte. This seems to be a very rough approximation. Still, this approach has been rather successful in reproducing and explaining observed trends in electrocatalytic reactions such as oxygen reduction [26, 30]

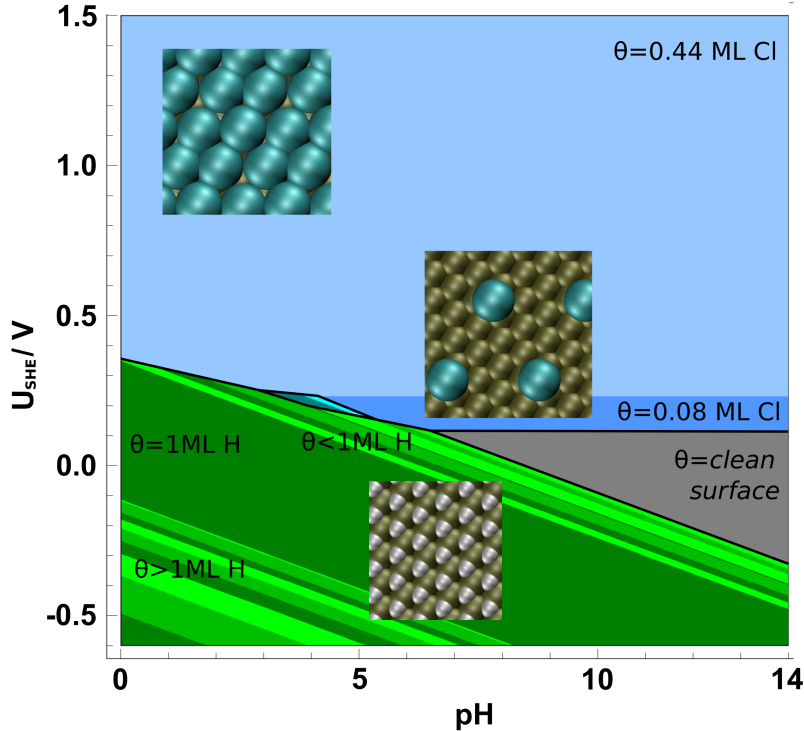


FIG. 3. Calculated Pourbaix diagram showing the stable phases of co-adsorbed chlorine and hydrogen on Pt(111) as a function of pH and electrode potential. The chlorine concentration corresponds to an activity of 0.1. (adapted from Ref. [29])

and hydrogen evolution [31] on metal electrodes. This is most probably a consequence of the good screening properties of metallic electrodes which make binding energies hardly dependent on applied electric fields [26, 32–34]. In addition, water typically interacts rather weakly with metal electrodes [35].

This concept will be illustrated using the coadsorption of protons and halides on Pt(111) [29]. As a first step, the energy of all possible co-adsorbate structures for various coverages needs to be calculated. Using these energies, phase diagrams of the surface coverages as a function of the electrochemical potentials of the solvated species can be constructed [29]. As the electrochemical potential is a function of the electrode potential and the concentrations of the solvated species, these phase diagrams can for example be converted into Pourbaix diagrams, i.e., phase diagrams as a function of pH and the electrode potential.

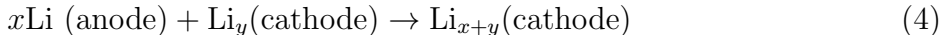
Figure 3 shows such a Pourbaix diagram for the co-adsorption of chlorine and hydrogen on Pt(111). This diagram is dominated by either pure hydrogen or pure chlorine adsorption

structures. Hence upon increasing the electrode potential, adsorbed hydrogen is replaced by chlorine. Thus the calculations confirm the competitive adsorption behavior of halides and hydrogen observed experimentally [36] which demonstrates the validity of this approach.

IV. ELECTRIC DOUBLE LAYERS AT BATTERY ELECTRODES

Up to now we have concentrated on the electric double layers at the interface between a metal electrode and an aqueous electrolyte, as they occur for example in electrocatalytic systems. However, EDLs evolve at any electrochemical electrode/electrolyte interface, also in batteries. The importance of this EDL, for example for the formation of the solid-electrolyte interphase (SEI), has been stressed before [37]. Here we want to address an aspect of the EDL which is important for the fundamental understanding of the operation of batteries and which can be based on macroscopic arguments [38, 39].

The operation of a battery is in principle rather simple. A battery consists of two electrodes, the anode and the cathode, which are separated by an electrolyte. The electrolyte is an ion conductor, but an insulator with respect to electron transport. It is important to realize that there must be a driving force for a battery to be operative. Let us now consider a Li-ion battery as an example. The driving force upon discharge is the energy gain upon the transfer of an Li atom from the anode to the cathode. However, the fact that the electrolyte only allows the transfer of ions forces the electrons to propagate through an external circuit where they can provide useful power. Eventually, at the cathode the Li-ion and the electron recombine. However, thermodynamically the specific reaction mechanism is irrelevant. Hence, the overall chemical reaction in a Li-ion battery describing the transfer of x Li atoms per suitable formula unit can be expressed as



The maximum voltage V_{OC} associated with this reaction, also called the open-circuit voltage (OCV), is given by the energy gain $\Delta G < 0$ divided by the number x of charge carriers [40]

$$V_{\text{OC}} = \frac{-\Delta G}{xF} , \quad (5)$$

where F is the Faraday constant. This corresponds to the difference in free energy of two well-defined charge-neutral configurations. Therefore it can rather easily be calculated by periodic density functional theory calculations [40, 41].

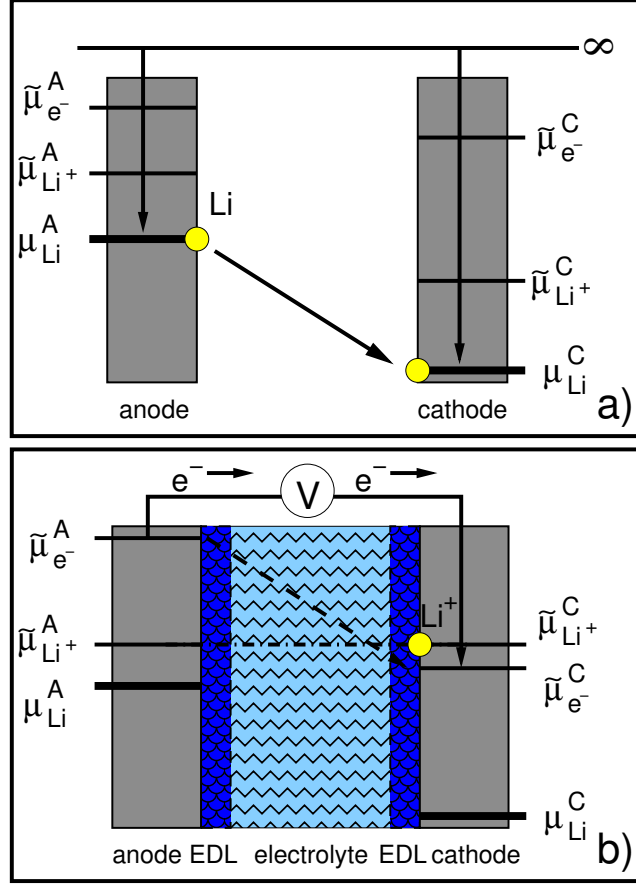


FIG. 4. Illustration of alignment of the electrochemical potentials in the anode and cathode of a battery. a) Cathode and anode not coupled to each other, b) cathode and anode connected through an electrolyte.

Alternatively, the open-circuit voltage can also be defined as the difference between the chemical potentials μ^A and μ^C of Li in the anode and the cathode, respectively [42]:

$$V_{OC} = (\mu^A - \mu^C)/e , \quad (6)$$

where e is the elemental charge. The corresponding schematic scenario is illustrated in Fig. 4a where the anode and cathode are assumed to be uncoupled. Note that the chemical potential of the Li atom can be decomposed into the electrochemical potentials of the Li ion and the electron,

$$\mu_{Li} = \tilde{\mu}_{Li^+} + \tilde{\mu}_{e^-} , \quad (7)$$

their levels are also included in Fig. 4a, where they are assumed to be given with respect to the vacuum level. Still, the particular values of the electrochemical potentials are not

directly related to the open-circuit voltage, hence from the electronic levels alone the OCV cannot be derived.

Now consider the scenario that an electrolyte is introduced into the battery cell. We disregard phenomena such as the formation of the solid-electrolyte interphase as they are not important for the following argumentation. As the electrolyte is an ion conductor, an equilibrium in the Li-ion distribution has to be established as long as the outer circuit is still open. Hence the electrochemical potentials of the Li ion in the anode and the cathode and in the electrolyte have to be the same. However, this means that now the open-circuit voltage can be expressed as

$$V_{\text{OC}}^{\text{el}} = (\tilde{\mu}_{\text{e}^-}^{\text{A}} - \tilde{\mu}_{\text{e}^-}^{\text{C}})/e, \quad (8)$$

where the subscript of $V_{\text{OC}}^{\text{el}}$ denotes the fact that the electrodes are connected through an electrolyte. Still the question arises: How do the electronic level re-align in such a way that the difference of their electrochemical potentials exactly equals the open-circuit voltage? This can only be explained by the formation of the electric double layers at both the anode and cathode upon establishing the equilibrium in the ion distribution. Their formation causes potential changes at the electrodes associated with electric fields that align the electrochemical potentials of the ions throughout the whole cell, but at the same time re-adjust the electrochemical potentials of the electrons in the anode and cathode in an opposite way such that their difference corresponds to the open-circuit voltage. This also means that the difference in the potential changes due to the formation of the EDL at the anode and cathode is directly related to the difference in the electrochemical potentials of the ions before the electrolyte is introduced.

V. CONCLUSIONS

Electrochemical electrode-electrolyte interfaces are associated with the formation of electric double layers. They can have a decisive influence on the chemical and/or electronic properties of the interface, and they are not only relevant in electrocatalysis, but also in electrochemical energy storage. However, the concepts used to describe the properties of electric double layers are still rooted in traditional macroscopic considerations. First-principles simulations are nowadays able to elucidate the atomistic and electronic structure of electric double layers, but as they are still computationally demanding, no complete microscopic

picture of the properties of electric double layers has emerged yet. We hope that through further atomistic studies such a complete picture can be achieved.

VI. DECLARATION OF INTERESTS

none

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