BUNSEN-MAGAZIN · 27. JAHRGANG · 5/2025

Axel Groß

Theoretical electrochemistry II: Modelling the electrochemical double layer

Electrochemical energy conversion and storage have become critical components within the energy transition towards a more sustainable future of our society [1]. Devices such as electrocatalysts, fuel cells and batteries play a central role in this transition. All these devices are characterized by the fact that processes at electrochemical interfaces are crucial in their operation which has caused a renewed interest in the research of these interfaces.

Interfacial electrochemistry is concerned with structures and processes at the interface between an electron conductor, the electrode, and an ion conductor, the electrolyte [2]. At such an interface between two conducting phases, a so-called electrochemical or electric double layer (EDL) forms. Note that the EDL as a whole has to be charge neutral in equilibrium, because if it was not, electrostatic forces would act on all charge carriers in the electrode and the electrolyte leading to a charge rearrangement until no net macroscopic electrostatic field exists outside the EDL.

Interestingly enough, our understanding of the structure of these interfaces is based on concepts that have been established more than one hundred years old [3–6], and it is fair to say that most of our current understanding of electrochemical interfaces is still based on these concepts [7]. This traditional understanding is illustrated in Fig. 1. Helmholtz was the first to realize that ions in the electrolyte will be attracted by charges in the electrode (see Fig. 1a), leading to a linear drop of the electrostatic potential within the *Helmholtz layer*. In contrast, Gouy [4] and Chapman [5] assumed a diffuse thermal distribution of the ions given by the Boltzmann distribution [2]. Since neither of the two models could explain all experimental observations, Stern combined both of them [6] resulting in a combination of linearly and exponentially decreasing electrostatic potentials within the double layer region, as illustrated in Fig. 1b.

There are limitations of the Stern model. The ions are considered to be point charges, the electrode is treated as a perfect conductor, and the explicit presence of the solvent molecules is treated on a continuum level. Still, the Stern model is often used as the basis for the discussion of the structure of the EDL [8–10]. It is interesting to note that our discussion of the structure of the EDL is still based on a model that is more than one hundred years old. This strongly suggests that this traditional model appears to capture the essence of the structure of the EDL. On the other hand, it is also known that the classical EDL model is not able to reflect the whole picture of even relatively simple electrochemical interfaces [9].

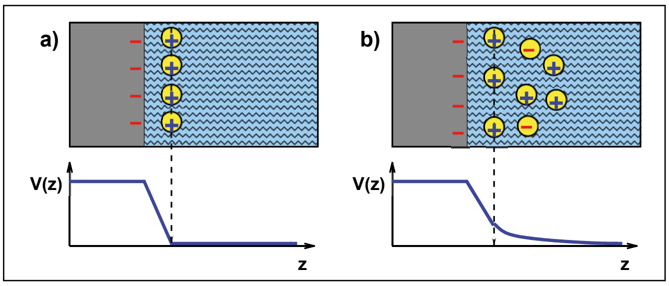


Fig. 1: Schematic illustration of the traditional understanding of the structure of electric double layers according to Stern [6] combining the Helmholtz model consisting of a charged electrode together with a layer of counter ions (panel a) [3] with the Gouy-Chapman model considering additionally the presence of a diffuse layer of anions and cations [4, 5].

The determination of the atomistic structure of the EDL is hindered by the fact that it typically corresponds to an electrochemical solid-liquid interface which means that the ions in the electrolyte are rather mobile and statistically distributed so that experimentally it is hard to resolve their positions. However, with respect to the atomistic modelling of electrochemical interfaces between an electrode and a liquid electrolyte, in recent years significant progress has been made [11], to a large extent due to the improvement in computer power, but also caused by conceptual progress and the development of suitable theoretical and computational tools.

It has now become possible to perform *ab initio* molecular dynamics (AIMD) simulations of electrode-electrolyte interfaces for reasonable system sizes and run times in order to derive meaningful statistical distribution. In Fig. 2, a snapshot is shown of an AIMD simulation of six-layers of water on a Pt(111) in a (6×6) unit cell comprising 144 water molecules [12] under the conditions of the potential of zero charge [13], i.e., for an ion-free water film on the uncovered electrode surface. Besides a snapshot of the simulation in the lower panel, the averaged electrostatic potentials of the metal-vacuum and the metal-water interface (upper panel) and the change of this potential caused by the presence of the water film are shown in this figure.

There are in fact some distinct differences compared to the schematic models of the EDL presented in Fig. 1. For example, the presence of the water film leads to changes in the electro-

Prof. Dr. Axel Groß
Institute of Theoretical Chemistry,
Ulm University, 89069 Ulm, Germany
Helmholtz Institute Ulm (HIU), Electrochemical Energy Storage,
89081 Ulm, Germany
axel.gross@uni-ulm.de

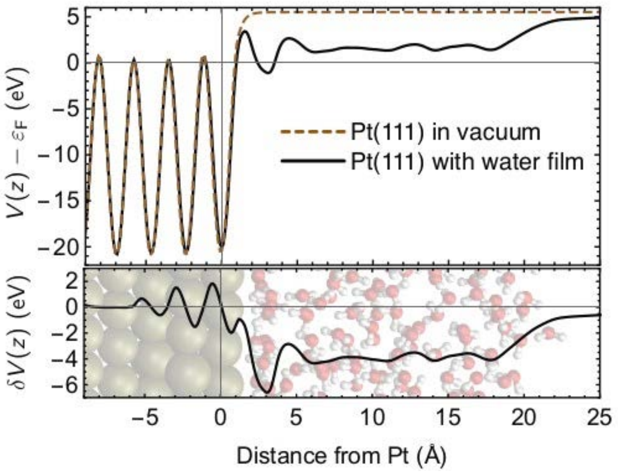


Fig. 2: Electrostatic potential V(z) of Pt(111) in a vacuum (dashed line) and the averaged potential of the Pt(111) electrode with an ion-free water film (solid line). The change caused by the water film δV(z) is illustrated in the lower panel. Reprinted from Ref. [12], with the permission of AIP Publishing.

static potential in the Pt(111) electrode up to the third layer, demonstrating that the assumption of an ideal metal is not fully adequate. Furthermore, there is an oscillatory structure in the electrostatic potential in the first water layers as a function of the distance from the electrode, reflecting the atomically layered structure of the aqueous electrolyte close to the electrode. From the second layer on, the electrostatic potential becomes rather flat, indicating that the widths of this EDL is below one nanometer. The electric field associated with the atomic variation in the first water layer is in fact much larger than the one associated with the overall potential drop from the metal electrode to the bulk water region.

In addition, an analysis of the charge distribution at the interface reveals that there is a significant electron transfer from the first water layer to the uppermost Pt layer [12]. Such a charge transfer has in fact also been observed for ice-like water layers on close-packed metal surfaces [14], independent of the orientation of the ice-like layers. Hence also at the potential of zero charge there is a significant charge rearrangement at metal-water interfaces. These observations call for a revision of our classical models of the electric double layer.

Interestingly enough, in the electrochemical community it is hardly explained why the EDL forms, i.e., the question of the driving force for its formation is not fully clarified. It is for example simply stated that an electric double layer forms whenever two conducting phases meet at an interface [2]. Furthermore, one finds explanations such as that the formation of excess positive or negative charges on solid surfaces upon contact with aqueous solutions gives rise to an electrical double layer as ions in the adjacent electrolyte rearrange to screen the charge [8]. First of all, this does not answer the question why charges form upon contact with the adjacent electrolyte. Second, this appears to be in conflict with the fact that at the so-called potential of zero charge also a double layer evolves associated with the separation of charges.

Sometimes it is helpful to consider neighboring scientific fields which are also concerned with interfaces. For example, a *p–n* junction or a metal-semiconductor contact in semiconductor physics can also be viewed as an electrochemical interface [15]. They are in fact also characterized by the formation of space-charge layers. These space-charge layers cause a potential drop across the interface. However, in semiconductor physics it is well accepted why these space-charge layers and the associated potential drop form: their presence aligns the Fermi levels of the p-type and n-type materials so that a constant Fermi level throughout the device results. It appears to be obvious that the same driving force should also be operative in the formation of EDLs at electrochemical interfaces in equilibrium, namely to align the chemical potentials of the electrons in the electrode and the electrolyte. Hence there is certainly still room for advancements in the conceptual understanding of electrochemical interfaces which could also reduce some of the confusion associated with the description of potentials in electrochemistry [16].

References

[1] R. Schlögl: The role of chemistry in the energy challenge, *ChemSusChem* 2024 **3**, 209-222.

[2] W. Schmickler, E. Santos, *Interfacial electrochemistry*, 2nd edn. Springer Berlin / Heidelberg, 2010.

[3] H. Helmholtz: Studien über electrische Grenzschichten, *Ann. Phys.*, 1897 **243**, 337.

[4] L.G. Gouy: Sur la constitution de la charge electrique a la surface d'un electrolyte, *J. Phys. Theor. Appl.*, 1910 **9**, 457.

[5] D.L. Chapman: A contribution to the theory of electrocapillarity, *Philos. Mag. Series 6*, 1913 **25**, 475.

[6] O. Stern: Zur Theorie der Elektrolytischen Doppelschicht, *Z. Elektrochem. Angew. P.*, 1924 **30**, 508.

[7] A. Groß, S. Sakong: Modelling the electric double layer at electrode/electrolyte interfaces, *Curr. Opin. Electrochem.* 2019 **14**, 1-6.

[8] M.A. Brown, Z. Abbas, A. Kleibert, R.G. Green, A. Goel, S. May, T.M. Squires: Determination of surface potential and electrical double-layer structure at the aqueous electrolyte/nanoparticle interface, *Phys. Rev. X*, 2016 **6**, 011007.

[9] J. Wu: Understanding the electric double-layer structure, capacitance, and charging dynamics, *Chem. Rev.* 2022 **122**, 10821.

[10] S. Ringe, N.G. Hörmann, H. Oberhofer, K. Reuter: Implicit solvation methods for catalysis at electrified interfaces, *Chem. Rev.* 2022 **122**, 10777

[11] A. Groß, S. Sakong, Ab initio simulations of water/metal interfaces: *Chem. Rev*. 2022 **122**, 10746

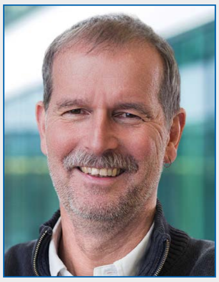
[12] S. Sakong, A. Groß: The electric double layer at metal-water interfaces revisited, *J. Chem. Phys*. 2018 **149**, 084705

[13] S. Trasatti: Structure of the metal/electrolyte solution interface: new data for theory, *Electrochim. Acta* 1991 **36**, 1659.

[14] S. Schnur, A. Groß: Properties of metal–water interfaces studied from first principles, *New J. Phys.* 2009 **11**, 125003

[15] S. Surendralal, M. Todorova, M.W. Finnis, J. Neugebauer: First-principles approach to model electrochemical reactions: Understanding the fundamental mechanisms behind mg corrosion, *Phys. Rev. Lett*. 2018 **120**, 246801.

[16] S.W. Boettcher, S.Z. Oener, M.C. Lonergan, Y. Surendranath, S. Ardo, C. Brozek, P.A. Kempler: Potentially confusing: Potentials in electrochemistry, *ACS Energy Lett*. 2021 **6**, 261.



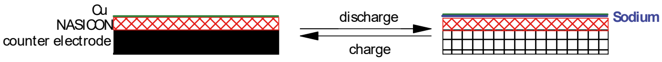
Prof. Dr. Axel Groß

Axel Groß studied physics at the University of Göttingen and got his Ph.D. in Theoretical Physics from the Technical University Munich in 1993. Afterwards he was a Post-Doc in the Theory Department of the Fritz Haber Institute of the Max Planck Society in Berlin before he became Associate Professor in Theoretical Physics at the Technical University Munich in 1998. Since 2004, he is Full Professor for Theoretical Chemistry at Ulm University, furthermore, in 2011, he became PI at Helmholtz Institute Ulm (HIU) Electrochemical Energy Storage. His research fields include theoretical chemistry, surface physics/chemistry and interfacial and bulk electrochemistry. His present research projects are mainly related to (electro-)chemical energy conversion and storage at interfaces and in bulk materials. From 2010 to 2016, he was spokesperson of the Research Unit FOR 1376 of the German Science Foundation "Elementary reaction steps in electrocatalysis: Theory meets experiment", and currently he is one of the three spokespersons of the Cluster of Excellence POLiS (Post-Li Energy Storage).

Spotlight on

Hot electrochemistry: Ceramics and solid ion conductors

In most electrochemical systems for energy conversion and storage as well as for synthetic processes, liquid electrolytes (solutions) provide the ionically conducting pathway between the electrodes. This applies even to technical processes in the electrolytic industry like production of aluminium or alkali metals. In electrochemical energy technology (EET), the numerous advantages of ionically conducting liquids like being cheap, readily available, highly conducting and having an ample supply are burdened with a major flaw: What happens in case of a leak? With nonaqueous solutions a further aspect is added: Flammability. These safety concerns have provided an additional driving force in the search for solid electrolytes. They may be safer in these regards, but they come with their own burden: Many of them show rather poor ionic conductivities at common temperatures of their desired application. A lot of research is dedicated to help by changing chemical composition and structure. An even more simple solution: Higher operating temperature. Perhaps not a universal one, but in many applications a realistic one: High temperature fuel cells running efficiently and stable even with less-than-perfect feed gas (containing traces of impurities deadly for many catalysts at room temperature) and water splitting on our way to green hydrogen, both with oxygen ion-conducting solid electrolytes. Both subjects are prominent in the research of the Ceramic Energy Converters group at the Fraunhofer-Institut für Keramische Technologien und Systeme IKTS in Dresden. Studies ranging from fundamental investigations of materials towards processing them into components and devices [1, 2] are among the many research activities dealing with the numerous facets of ceramics going all the way to e.g. EET. Some of the studied materials hold promise also at ambient temperatures in e.g. solid-state sodium batteries [3]. In an all-solid zero-excess sodium cell with a NASICON solid electrolyte, a copper current collector providing the negative electrode (where sodium is deposited during charging) was combined with an all-sodium counter electrode (instead of a storage material in a real cell) in a study to establish best surface properties of the NASICON for stable adherence of the copper current collector as well as the despoited sodium layer in the charged state.



[https://www.ikts.fraunhofer.de/de/abteilungen/energiesysteme/werkstoffe_komponenten.html]

References

[1] R. Anton, A. Lowack, D. Wagner, J. Schilm, M. Kusnezoff, *J. Europ. Ceram. Soc.* 2025 **45**, 117163.

[2] M. Kusnezoff, M. Jahn, S. Megel, S. Rothe, S. Hielscher, E. Reichelt, N. Trofimenko, G. Herz, W. Beckert, J. Schilm, A. Rost, J. Schöne, G. Ganzer, D. Wagner, L. Nousch, V. Sauchuk, M. Hartmann, A. Michaelis, *ECS Trans*. 2021 **103**, 307-326.

[3] A. Lowack, P. Grun, R. Anton, H. Auer, K. Nikolowski, M. Partsch, M. Kusnezoff, A. Michaelis, *Batteries&Supercaps* 2024 **7**, e202400364.