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Review Article

Electric double layer of Pt(111): Known unknowns and unknown knowns

Katharina Doblhoff-Dier and Marc T. M. Koper

Abstract

The electric double layer is one of the most fundamental concepts in electrochemistry. Nevertheless, its exact structure is still often unresolved. In this contribution, we discuss what we, at present, believe to know and what we believe not to know about the structure of the Pt(111) double layer close to the potential of zero charge (pzc). To this end, we discuss and compare several models put forward in the last few years in order to explain recent (and less recent) experimental observations. Through a discussion of several models, we conclude that water adsorption at the interface likely plays an important role in correctly interpreting capacitance features observed close to the pzc. The capacitance features at low electrolyte concentration, which show important deviations from Gouy-Chapman diffuse layer theory, are, to date, not yet resolved beyond doubt, but we critically analyze and compare the various models that have been put forward to model the interface. We thereby point out weaknesses in the models as well as similarities and differences between the models.

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Keywords

Electric double layer, Double-layer capacitance, Pt(111), Interfacial water, Gouy-Chapman.

Introduction

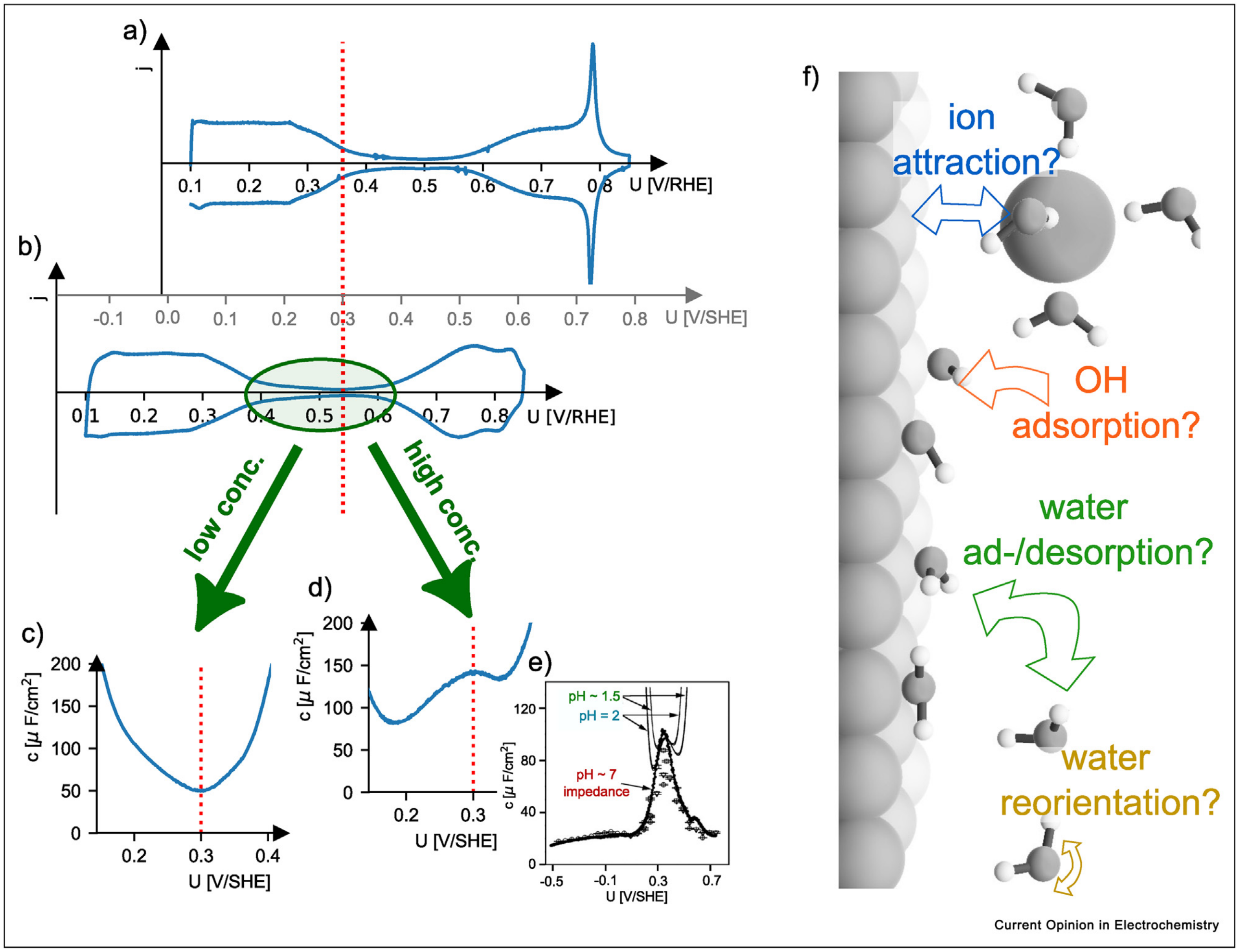
At the interface between a charged electrode and a (liquid) electrolyte, electrons, ions and solvent molecules form a structure that is typically referred to as the *electric double layer*. The structure of this double layer has a direct impact on capacitive energy storage and can influence (the rate of) electrochemical reactions. Consequently, the electric double layer has been a topic of central interest in electrochemistry since the early days of electrochemistry [1,2]. In this paper, we want to focus on recent insights into the double-layer structure of Pt(111) — the “Guinea pig” of electrochemical surface science. Our special attention lies on the (current) interpretation of Pt(111)’s capacitive behavior near the potential of zero charge (pzc). In the discussion, it will become clear that the behavior of the Pt(111)/electrolyte interface cannot be readily captured by classical models, such as the Gouy-Chapman-Stern (GCS) model. Extensions or modifications of this simple picture are necessary, but — in spite of decades of research as well as interesting results obtained in the past few years — we still do not know the origins of these deviations with certainty. Several interpretations have been put forward (see Figure 1) and we will critically discuss the most prominent ones. In doing so, we will also challenge some of the common assumptions made in electrochemistry and scrutinize the evidence they are based on.

The paper is organized as follows: In the first part, we will discuss the capacitive behavior of Pt(111) at low electrolyte ion concentrations, close to pzc, where we expect the capacitance to be dominated by the diffuse Gouy-Chapman layer. This discussion will raise the question of what we mean exactly by “non-specifically adsorbing” ions and whether they really exist in relation to Pt(111). In the second part of the paper, we will focus on the capacitive behavior of Pt(111) at higher concentrations, where we expect the capacitance to be dominated by the inner layer. In this context, we will discuss competing interpretations of the capacitance based on water either reorienting or chemisorbing to the metal. We will discuss the evidence on which these interpretations are based and examine the reliability of the underlying simulations.

Capacitance of Pt(111) at low concentrations

In Figure 1a, we show a typical cyclic voltammogram (CV) of Pt(111) taken at pH = 1 in a 0.1 M $HClO_4$

Figure 1



Current Opinion in Electrochemistry

(**a**) CV of Pt(111) in 0.1 M $HClO_4$ (pH = 1); (**b**) CV of Pt(111) in 0.1 mM $HClO_4$ (pH = 4); (**c**) zoom-in of b; (**d**) similar to c, but for an electrolyte containing 0.1 mM $HClO_4$ + 5 mM $NaClO_4$; (**e**) Capacitance peak found by Pajkossy and Kolb (Reprinted and adapted from Ref. [3], Copyright (2003) with permission from Elsevier). (**f**) overview of effects suggested to play a role in the interpretation of the Pt(111) CVs close to pzc. (Data in (**a**) to (**d**) taken from Ref. [4]).

electrolyte. The accepted interpretation of this CV is that there is an H-adsorption region at $0 < E < 0.4V_{RHE}$, an OH-adsorption region for $0.6 < E < 0.85V_{RHE}$, and a double-layer region in between.

In the case of Pt(111), this assignment is supported by theoretical and computational results: static DFT calculations suggest the H- and OH- adsorption regions to be well separated [5,6] and simulated CVs taking only H-adsorption into account can reproduce the shape of the CV in the H-adsorption region to a high degree of accuracy [6–8]. This comparison with theory is relevant as other CVs, such as that obtained for a monolayer of Pd on Pt(111), look very similar to that of Pt(111) but do *not* have a separate H and OH-adsorption region [9].

If the H and OH adsorption region are well separated on Pt(111), this suggests the presence of an ideally polarizable, adsorbate-free region in between. If the pzc also lies in this region (which is expected to occur at pH = 3 and pH = 4, see Figure 1b), a so-called Gouy-Chapman minimum is expected in the double-layer capacitance at low ion concentrations. However, as Cuesta put it in 2004 [10] "Although many efforts have been devoted to the search of the Gouy–Chapman minimum in the double layer capacitance curve of Pt(111), they have all been unsuccessful." [3,10]. This puzzled electrochemical surface scientists for decades.

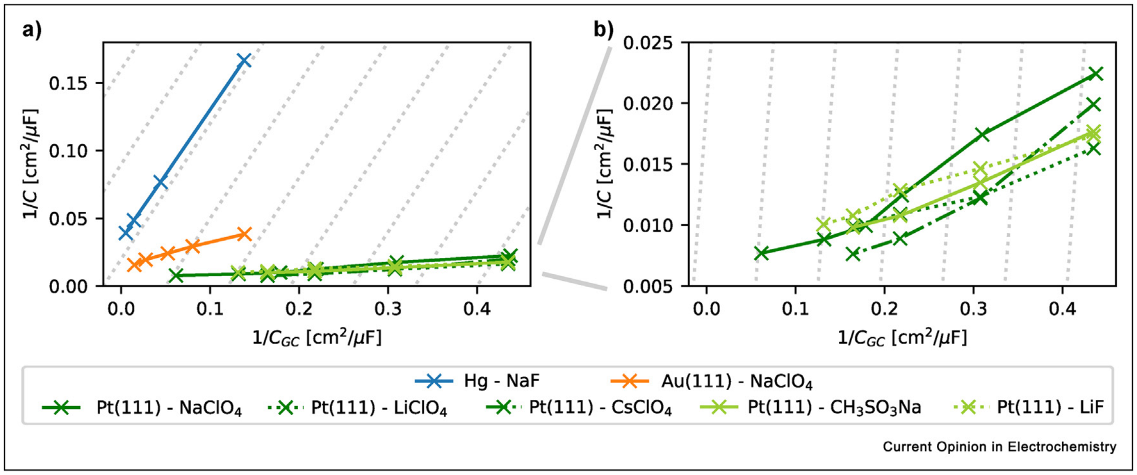
In 2020, Ojha et al. [11] finally found a capacitance minimum close to the expected pzc (see Figure 1c). This capacitance minimum had previously been "overlooked", as it only shows up for electrolyte concentrations in the 0.1 mM range. Although the Gouy-Chapman minimum can thus be found, the so-called Parsons-Zobel [12] plots (see Figure 2b) of the measured capacitance data still deviate from GCS theory. According to GCS theory, the slope in the Parsons–Zobel plots should be 1, but in the case of Pt(111), the slope is much smaller (see Figure 2b). This indicates that the part of the capacitance that is typically assigned to the diffuse layer capacitance C_{GC} is *larger* than expected, (although it does appear to scale with the ion concentration as predicted by Gouy and Chapman [2]).

Deviations in the Parsons–Zobel plots from the ideal behavior are not uncommon and have been explained earlier by either surface roughness or a weak (an)ion adsorption [12–15]. While surface roughness can be excluded on a well-defined Pt(111) surface, there may be a case for ion adsorption. However, there is 1) no sign of site blockage, excluding strong chemisorption, 2) previous experimental results suggest that ClO_4^- does not adsorb specifically (at least not in the potential window of interest) [16] and 3) the minimum in capacitance was not observed to shift significantly with increasing concentration [11], which — according to conventional wisdom — is a sign of the absence of (specific) adsorption [15]. The interaction of the ions with Pt(111) would thus have to be sufficiently weak in order not to show up directly, while, at the same time, being sufficiently strong to cause Parsons–Zobel slopes that are much smaller than those observed for other single crystal surfaces.

To answer the question of whether a weak ion–surface attraction can really explain the experimental results, two models have been put forward independently from each other by the authors of the present paper [17] and by Schmickler [19]. Both models build on mean-field theory, but Schmickler describes the (an)ion adsorption via an adsorption isotherm, while we described the interaction of the ions with the surface via an attraction potential. The models agree in that they predict a relatively weak ion–surface interaction of a few 100 meV to be sufficient to explain the strongly reduced Parsons–Zobel slopes observed experimentally (see also supporting information). The semi-quantitative agreement between the models can be explained intuitively by the fact that the Langmuir isotherm follows an exponential behavior at low coverages, similar to what is caused by an attractive potential. A more detailed discussion and a mathematical derivation of this correspondence is given in the supporting information.

The main difference between the models therefore lies in the interpretation of the model, rather than in the numerical results: While Schmickler considers anion adsorption only, our model explicitly includes the possibility of anion *and* cation attraction to the surface. In fact, while an anion attraction of this strength would not necessarily cause a considerable shift of the potential at which the capacitance minimum occurs with increasing ion concentration (in accordance with the experimental data [17]), some experimental observations can be explained better if not only anions but also cations are assumed to be attracted to the surface [17]. In this context, it is important to discuss what exactly we mean by specific adsorption. The predicted adsorption strength of a few 100 meV seems rather weak for chemical bonding. Additionally, if the adsorption is really the formation of a chemical bond to the surface, then the model by Schmickler would predict a surface coverage of approximately 0.25 for 0.1 M solutions at a

Figure 2



(Figure reproduced from Ref. [17] CC-BY-NC-ND.): Parsons–Zobel plots obtained in experiments at pH = 3 for Au [11], pH = 4 for Pt [4,11], and pH = 7.1 for Hg [18]. Panel (**b**) shows a zoomed-in version of panel (**a**), focusing on the region of interest for Pt(111). Dotted gray lines: slope = 1, corresponding to the predictions of the Gouy-Chapman-Stern model. (Data for Au and Pt is reproduced from Ref. 11 with additional data added from Ref. [4]; data for Hg is taken from Ref. [18]).

potential of 0.1 V vs. pzc (see Fig. S1). It seems unlikely that such a high ion coverage would go unnoticed [20]. On the other hand, the predicted interaction is much stronger than what may be expected from an image charge interaction ($\sim$10 meV). Finally, the presence of a water-mediated ion interaction as recently proposed to play a role in CO_2 reduction [21], would yet have to be proven for adsorbate-free surfaces. In our opinion, the exact nature of the attraction is therefore unknown at present. Consequently, also the question of whether anions and/or cations are attracted to the surface remains open.

Independently of whether anions and cations are attracted to the surface or whether it is only the anions that adsorb, the interpretation of the data as a consequence of ion adsorption leaves a few open questions. For example: Why is this interaction apparently stronger on Pt(111) than on other single crystal surfaces or mercury? Why is it similar for all investigated electrolytes (see Figure 2 and discussion in Sec. S.1.1 in the supporting information)? And why are there no signs of specific adsorption if the adsorption strength is $\sim$100 meV? Although the last question can be circumvented by assuming that the ions do not directly adsorb to the surface or by assuming a low maximum ion coverage, the other two questions leave room for more research — or an alternative interpretation.

One such alternative explanation was put forward recently by Huang [22], who considered OH adsorption rather than ion adsorption/attraction to cause the observed deviations from the ideal Parsons Zobel plots. Huang fitted an energetic distribution of H and OH adsorption sites to the CV data and could obtain good fits to the data around the pzc when assuming $\sim$5% of the adsorption sites to have an equilibrium potential for adsorption in the potential range that is typically ascribed to the double-layer region. The good fits should not be overrated, however, as, in principle, any CV curve can be fitted by assuming an appropriate distribution of adsorption sites of any arbitrary species. We therefore consider it more important to question whether the results of the fitting procedure are chemically plausible. This requires further analysis of the results presented by Huang's model, as given in the supporting information. Here, we only summarize the main points that require attention, as well as our final conclusion: The first question that requires attention is: "What is the nature of these 5% of adsorption sites on single-crystalline Pt(111) that have a lower equilibrium potential than the rest?" The second is "Why is the distribution of adsorption sites ion concentration dependent?" (Without this dependency Huang's model would predict a Parsons–Zobel slope of 0). Although we propose some viable explanations for both questions in the supporting information, we believe that the hypotheses put forward in the model require further experimental testing and/or computational modeling in order to confirm or confute the assumptions underlying the model.

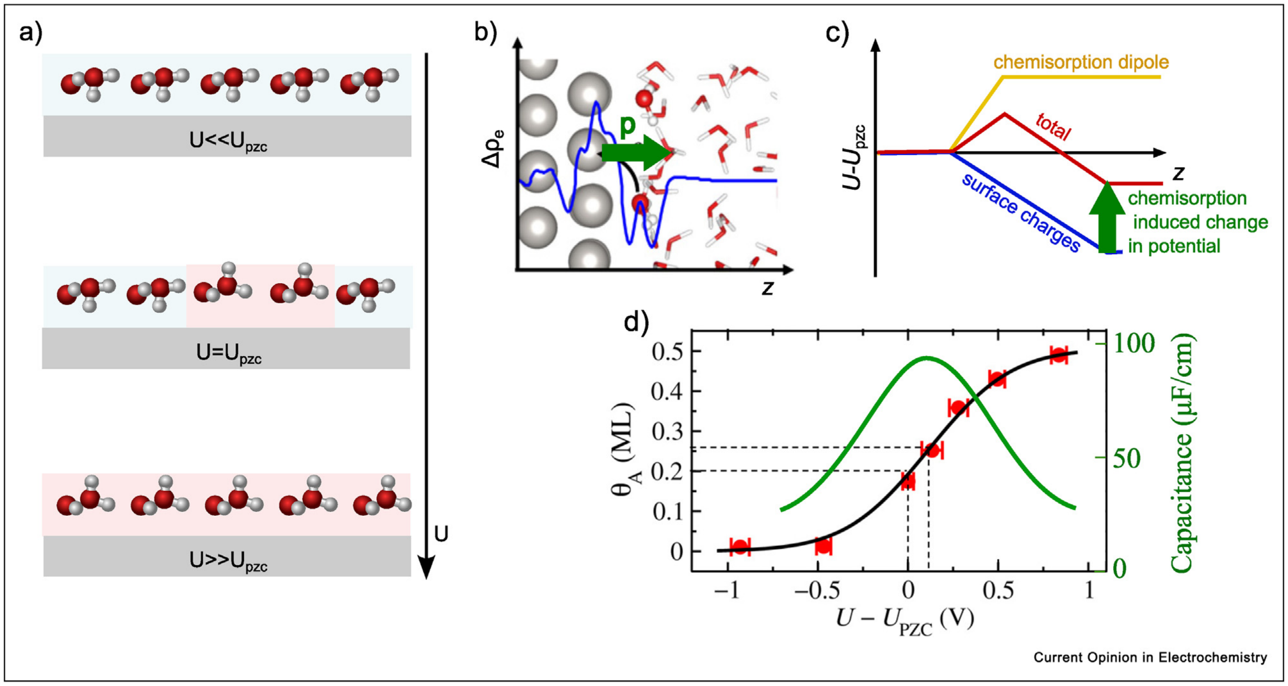
Taken together, there are thus three competing explanations for the deviations of the Pt(111) capacitance from the ideal behavior at low ion concentrations: (1) anions adsorb weakly, (2) anions and cations are attracted to the surface but do not adsorb or (3) Pt(111) does not have a true double-layer region. All explanations are plausible to a certain extent, but in all cases, some questions remain. Further measurements are clearly needed to confirm or confute the models proposed.

Although the deviations from the Parsons–Zobel plots only show up at low electrolyte concentrations, the underlying mechanism will very likely also be at play at higher, experimentally more relevant concentrations. The mechanism is thus not only of academic interest, but may easily influence reactions under more realistic conditions.

Capacitance of Pt(111) at high electrolyte concentrations

Once the electrolyte concentration is high enough, we expect the double-layer capacitance to be dominated by what would traditionally be called the "inner layer" capacitance. The Gouy-Chapman minimum discussed in the previous section can then not be observed anymore. Instead, we observe a peak close to the pzc (see Figure 1c) [4,11]. This prominent ($> 100 \mu F/cm^2$) and sharp (few 100 mV wide) peak was first observed by Pajkossy and Kolb in 2001 [24] (see Figure 1e), who attributed it to water reorientation [3]. This interpretation is inspired by early double-layer models, which described the interfacial water layer via dipoles that can have two orientations, H-up or H-down (as indeed found for water-ice bi-layers on Pt(111) [25]). At potentials far below pzc, all dipoles will have an H-down orientation, but close to pzc, more and more dipoles will flip their orientation leading to a peak in capacitance close to pzc (see Figure 3a). As the potential is further increased, the capacitance will decrease again as saturation is reached (i.e., as all dipoles have H-up configuration and no more dipoles can flip sign) [26]. Numerous variants of such two (or few) state models have been put forward since the early 1960s (e.g. Refs. [26–28]) and most of them predict a strong capacitance peak in a limited potential range. A similar 4-state model developed by Parsons [29] has been used successfully to fit the inner-layer capacitance of Ag(100) [30]. The capacitance peak on Ag(100) is strongly reminiscent of that found on Pt(111), suggesting that a similar fit should be possible for Pt(111). Further evidence supporting the idea of water reorientation as cause for the capacitance peak on Pt(111) stems from FTIR measurements and temperature jump experiments, which both indicate a changing water orientation

Figure 3



Current Opinion in Electrochemistry

(**a**) schematic representation of a 2-state model capturing water reorientation at the interface as a function of applied potential; (**b**) chemisorption-induced charge redistribution and the induced dipole (adapted from Ref. [23] under a CC BY-NC 4.0 license); (**c**) schematic drawing of the chemisorption-induced change in potential; (**d**) coverage of chemisorbed water θ_A as a function of potential (red dots) overlain with the capacitance as obtained by the model by Le et al. [23] (adapted and remixed from Ref. [23] under a CC BY-NC 4.0 license).

at pzc [31,32]. However, without further evidence, it remains unclear whether 1) a few-state model as sketched above is not too simplistic and whether 2) the water reorientation really causes a capacitance peak (the peak width and height predicted by the models depend sensitively on the dipole−dipole interactions [26,33]). To answer these questions, it is interesting to turn to results from ab-initio molecular dynamics (AIMD) simulations of the (electrified) Pt/water interface.

AIMD simulations indeed predict a rather bimodal water structure with water dipoles either pointing more up or more downwards [34,35]. A two-state model thus seems justified. A more detailed look, however, reveals that there are actually three types of water: a chemisorbed species that lies nearly flat on the surface with both H-atoms slightly up-tilted, and, slightly further away from the surface, water molecules pointing one H-atom either up or down.[1] Importantly, the chemisorbed water molecules carry a dipole that is not only caused by their orientation, but also by a bond-induced electron rearrangement leading to a strong chemisorption dipole pointing away from the surface (i.e., the water molecule “donates” electrons towards the surface) (see Figure 3b) [35,37,38]. Additionally, the surface coverage with chemisorbed water is potential dependent [23,36,39][2] and increases from 0 at low potentials to 0.2 at pzc and 0.5 at high potentials with the strongest increase in coverage observed close to pzc (see Figure 3d) [23]. The potential drop caused by the chemisorption dipole (schematically shown in Figure 3c) is a non-negligible effect. At pzc, it is even the dominant effect leading to the workfunction decrease of the Pt(111)/water interface compared to the Pt(111)/vacuum interface [35]. Extrapolating the potential drop computed at pzc (∼ 1.3 V for a coverage of $\theta = 0.2$) [35] linearly to full coverage ($\theta = 0.5$), the chemisorption dipole causes a maximum potential drop of more than 3 V. This has to be put into relation to the work function change incurred when switching from a H-down bilayer to an H-up bilayer (∼ 2 V [45], note, however, that an ice-like

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[1] As the ratio of H-up vs. H-down molecules [36] also depends on the potential, one may be tempted to believe that this situation can still be captured by Parsons 4-state model. This is not true, though. 1) The orientation of the water molecules is also influenced by the potential [36], 2) Parsons did not consider a maximum coverage of the adsorbed water in his model and 3) Parsons did not consider the chemisorption dipole.

[2] The results by Le et al. [23] were obtained with PBE-D3, those from Ref. [36] with RPBE-D3. It is, in our opinion, an important observation that the water ad-/desorption behavior observed with PBE-D3 can be reproduced even quantitatively with RPBE-D3, as PBE-D3 is known to underbind H_2O on the Pt(111) surface (adsorption energy $E_{ad}^{\text{PBE-D3}} = 0.49$eV for PBE-D3 [40], while $E_{ad}^{exp} = 0.57$eV [41]) and to show an incorrect wetting behavior for water on Pt [42]. Furthermore, PBE-D3 over-structures water [43] even at elevated temperatures (see supporting info of Ref. [44]). Many of these characteristics are improved for RPBE-D3 (e.g., $E_{ad}^{\text{RPBE-D3}} = 0.60$eV).

water bilayer is a very crude approximation of surface-near water). Based on this comparison, one may conclude that the chemisorption-induced polarization effect could have a considerable effect on the capacitance peak observed on Pt(111). In Ref. [23], Le and coworkers even considered this to be the only effect and modeled the capacitance peak as purely due to water adsorption (their peak is somewhat too broad though - see Figure 3d) [23].

Taken together, there are thus two competing interpretations for the inner-layer capacitance peak on Pt(111) close to pzc: a) the peak is caused by a water reorientation and b) the peak is caused by a chemisorption dipole of water, the adsorption isotherm of which has its maximum change in water coverage close to pzc. A third option c) are ion crowding effects. Although we believe it unlikely that ion crowding effects are the main player in causing the capacitance peak (for silver maximum ion concentrations as low as 2 M would be required to capture the peaks semi-quantitatively) [46], they may certainly contribute. Overall, to our knowledge there is, so far, no conclusive evidence on which effect is stronger or dominant.[3] In a recent publication, Wang et al. [47], studied the capacitance on Ag(111), which, again, shows a capacitance peak somewhat reminiscent of that on Pt(111). Wang et al. [47] fitted a (field-dependent) dielectric constant to the experimental data and compared the results to the predictions from (modified) Kirkwood-Booth theory for the field-dependent saturation of the dielectric constant of water [48]. The fit that they obtain is overall good except for low field strength, where the dielectric constant extracted from the experiment considerably overestimates the predictions from Kirkwood-Booth theory. One may thus postulate that this “additional” polarizability is caused by water adsorption (which is indeed also observed for Ag), suggesting a cooperative effect of water reorientation and water chemisorption to form the capacitance peak.

To establish the origin of the capacitance peak on Pt(111) with more certainty, it will be interesting to analyze the capacitance on Pt(111) with a similar approach as that by Wang et al. [47] Additionally, it would be interesting to investigate the inner-layer capacitance in a wider pH range: At low pH, the presence of adsorbed hydrogen should prevent the adsorption of water at the pzc [49,50].[4] If water adsorption and the concomitant increase in chemisorption dipole play a role in creating the capacitance peak at pzc, one would expect the peak in the double-layer capacitance to diminish. Unfortunately, the fast hydrogen adsorption dynamics make it impossible to measure the double-layer capacitance at low pH and pzc experimentally, rendering this test difficult. At high pH values, when the pzc falls into the OH adsorption region, the capacitance peak is not expected to diminish, as adsorbed OH does not seem to block water adsorption [51]. Therefore, while it would be interesting to know the behavior of the double-layer capacitance at pzc in a wide pH window, we currently do not see how the relevant region of low pH could be accessed experimentally.

For the time being, we believe that both explanations, water reorientation and water adsorption, should be considered as, likely, it is a combined effect and the relative importance of one effect or the other may depend on the metal surface considered. A more detailed investigation of the capacitance curves not only on Pt(111), but also on various Ag surfaces and Au(100) [52,53] (all of which show a pronounced peak in the inner-layer capacitance) would therefore be of interest. In the same way, it would be of interest to consider those electrodes for which no (strong) peak is found (e.g., mercury [18]) and to investigate in which way the water structure is different on those surfaces such that no water reorientation/water chemisorption peak is visible in the inner-layer capacitance.

Conclusion

In this contribution, we discussed the capacitive behavior of Pt(111) and the (possible) atomic scale interpretations thereof. Since the 19th century, models have been put forward that describe the physical processes occurring at the interface during double-layer charging. However, for Pt(111) electrodes close to the pzc, these traditional models are incomplete. The past three years have brought important developments and new, more elaborate and (hopefully) more realistic, models have been put forward that substitute or add on traditional models.

In particular, for Pt(111) strong deviations from the (traditional) Gouy-Chapman-Stern model have been observed experimentally [11]. Several models have been put forward that attribute these deviations to an attraction of anions/cations to the electrode surface [17,19]. These models, as well as other options (e.g., the adsorption of anions or OH species) [22] are critically assessed in the main text and we conclude that at least two of the models are very similar in spite of using different approaches.

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[3] We note that this information must be extractable from the AIMD simulations, as long as one trusts the chemisorption-induced charge transfer as well as the water structure obtained in these general gradient approximation-based DFT simulations.

[4] In this statement, we do not follow the suggestion made by the authors of Ref. [49] who suggested that their results may be affected by a DFT-error and that water should adsorb at 1/3 of a monolayer. The reason for disregarding this suggestion is threefold: 1) The suggestion was made based on a comparison of DFT-MD data with experimental data at pH = 1. The pH is, however, not defined in the simulations and neither is equilibration of the H-coverage reached. Such a comparison therefore seems treacherous. 2) As discussed in footnote 1, RPBE-D3 is expected to perform rather well for the description of the Pt/water interface.

Pt(111) also shows peculiarities in what is usually ascribed to the inner-layer capacitance. The strong and narrow peak in the inner-layer capacitance has long since been attributed to water reorientation [3,24]. As argued in the text, we believe that this traditional picture should be interpreted in a broader sense. DFT and ab-initio molecular dynamics simulations [23] suggest that not only the orientation of water molecules, but also their chemisorption dipole plays a major role: it influences the water chemisorption isotherm and the surface potential drop. This observation suggests the idea of pure water reorientation to be oversimplified while suggesting an additional molecular process to partake in the capacitance peak.

In spite of recent advancements, the double-layer structure of Pt(111) is not completely understood yet. For example, the relative importance of water reorientation and water chemisorption to the capacitance peak is so far unclear. Additionally, the models put forward to explain the deviations from the Gouy-Chapman-Stern behavior lack a chemical motivation, making it hard to decide which model is more credible (or whether all mechanisms may be at play together).

We believe that the true double-layer structure can only be unraveled if theory and experiment work hand in hand. On the experimental side, detailed X-ray studies of the Pt/electrolyte interface may shed more light on the presence of ions close to the surface. On the theory side, advanced multi-scale models as well as machine learning approaches may allow the simulation of realistic interfaces at experimentally relevant ion and proton concentrations — a necessary prerequisite when investigating ion–surface interactions. Additionally, to achieve quantitative agreement between models and experiments, further development on the DFT side (to mitigate charge transfer errors, band alignment problems and errors in the adsorption energies at acceptable computational cost) will prove relevant (e.g., to establish without doubt whether water reorientation or chemisorption is more relevant or to investigate whether Pt(111) possesses a true double-layer window). Overall, we believe that resolving the true interfacial structure at a Pt(111) surface is a multidisciplinary challenge that has not seen its last developments yet.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.coelec.2023.101258.

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* of special interest
* * of outstanding interest

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This experimental + theory paper presents capacitance measurements for Pt(111) @ pH = 4 close to pzc for various different electrolyte, showing that the slope obtained in the Parsons–Zobel plots is independent of electrolyte. Theoretical work is used to qualitativiely interpret the shape of the CVs close to pzc and the Parsons–Zobel plots as a consequence of ion attraction to the surface with ions approaching the surface up to the hydrated ion size and of water adsorption.

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