Progress and pitfalls in measuring the double-layer capacitance of platinum electrodes

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Review Article

Progress and pitfalls in measuring the double-layer capacitance of platinum electrodes

Nicci L. Fröhlich and Marc T. M. Koper

Despite extensive research, the double-layer structure at Pt/aqueous electrolyte interfaces (quantified by the double-layer capacitance, C_{dl}) remains incompletely understood as even for the model Pt(111)/$HClO_4$ interface, anomalous C_{dl} trends have been reported. These trends were previously ascribed to differences in measurement techniques (*i.e.* dc methods such as cyclic voltammetry versus ac methods such as electrochemical impedance spectroscopy [EIS]). However, by repeating these measurements using EIS, we clarify that these anomalous C_{dl} trends are not measurement artefacts but instead reflect intrinsic properties of the Pt(111)/$HClO_4$ interface, necessitating continued investigation. We further highlight the complexity introduced by electrosorbed H_{ads} and/or OH_{ads} species resulting from catalytic H_2O dissociation, which contribute an adsorption (pseudo)capacitance, C_{ads}. This complicates the deconvolution of C_{dl} from total capacitance, a challenge further exacerbated by structure-dependent adsorption between different Pt facets. Our goal is to clarify how these factors affect capacitance interpretation at Pt/aqueous electrolyte interfaces, particularly highlighting the progress and challenges in accurately extracting C_{dl} values from prior studies.

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Introduction

Despite extensive study, a precise fundamental understanding of the electrical double-layer (EDL) structure at the platinum/aqueous interface remains limited. A key parameter for elucidating the EDL structure is the (differential) double-layer capacitance, C_{dl}, which quantifies the (potential-dependent) accumulation of ions and/or reorientation of solvent molecules at the interface. In nonspecifically adsorbing $HClO_4$ electrolyte, Pt(111) is the only Pt facet to exhibit a true double-layer window (0.40–0.60 V_{RHE}) where the surface is adsorbate free and ideally polarisable [1,2]. Outside this potential window, the pseudocapacitance (C_{ads}) contributed by the electrosorption of H_{ads} or OH_{ads} from H_2O dissociation in the hydrogen (H_{upd}, 0.05–0.40 V_{RHE}) and hydroxyl adsorption (OH_{ads}, 0.60–0.85 V_{RHE}) regions, respectively, nontrivialises the direct quantification of C_{dl} from the total capacitance [3–5]. This is particularly relevant in the context of the lower-coordinated Pt facets (*i.e.* (110) and (100)) that are more active for H_2O dissociation. As a result, at any given potential, all Pt surfaces (except for Pt(111) in the double-layer window) are always covered in H_{ads} and/or OH_{ads} (*i.e.* are never adsorbate free), such that C_{dl} cannot be measured directly [6–10].

Following the early work of Pajkossy and Kolb [2], there has been renewed interest in the measurement and interpretation of the C_{dl} of platinum electrodes, both from the experimental and computational point of view [11,12]. Zhang and Huang have recently provided a useful summary of the existing controversy about the various experimental C_{dl} values of platinum (single-crystal) electrodes reported in the literature and their measurement reliability [13]. In this article, we address some of the experimental issues in measuring the C_{dl} of platinum, with a particular focus on the influence of electrode surface structure and the measurement technique, especially the choice of equivalent circuit when fitting electrochemical impedance spectroscopy (EIS) data. For Pt(111), we highlight the importance of accounting for nonideal frequency responses, while for other surfaces, including polycrystalline Pt, we emphasise the role of structure-sensitive pseudocapacitive processes in interpreting total capacitance. In this article, we do not deal with the physical interpretation of the C_{dl} values; for a discussion of these aspects, we refer to the recent literature [12,14].

Measurement of C_{dl} in the absence of specific adsorption

Zhang and Huang recently highlighted a discrepancy regarding the double-layer capacitance, C_{dl}, of Pt(111)

measured in the double-layer window (0.40−0.60 V_{RHE}, SI Figure 3a) [13]: using EIS, C_{dl} was measured to be 20−65 μF cm^{-2} in 0.1 mM $HClO_4$ + 0.1 M $KClO_4$ [2], compared to 100−200 μF cm^{-2} in 0.1 mM $HClO_4$ + 5 mM $LiClO_4$ using cyclic voltammetry (CV) [15]. These values appear inconsistent with the Gouy−Chapman (GC) theory, which predicts a larger differential capacitance for increasing bulk ion concentrations around the potential of zero (free) charge (PZC; ∼0.30 V_{SHE}, or 0.54 V_{RHE} in pH 4, for Pt(111) in $HClO_4$) [1,16]. As measured previously by Ojha et al. [15], the capacitance response was found to be independent of cation identity; therefore, such an inconsistency with the GC theory cannot be explained by differences between using Li^+ or K^+.

Zhang and Huang attributed this apparent anomaly instead to the electrochemical measurement technique used (*i.e.* CV versus EIS) [13,17], where CV calculates C_{dl} by normalising the current-to-scan rate and EIS uses an ac potential perturbation to separate C_{dl} from other elements describing the interfacial response by fitting with an appropriate electrical equivalent circuit (EEC). However, this separation only works if the different capacitive responses of the interface occur on sufficiently different timescales [18,19].

In principle, CV and EIS should yield the same C_{dl} values in the double-layer window of Pt(111) in $HClO_4$ (0.40−0.60 V_{RHE}) because no adsorption takes place. However, we recently showed there is a small, but nontrivial, scan-rate or frequency dependence in the C_{dl} values obtained by these techniques [20]. Therefore, the capacitance response in the double-layer window of the Pt(111)/$HClO_4$ interface is more appropriately modelled by an EEC comprising a resistor (solution resistance) connected in series with a constant phase element (CPE, Q_{dl}) rather than an ideal capacitor (Figure 1a). The origin of this CPE behaviour remains heavily debated as an EEC ultimately only provides an empirical analysis of EIS data such that its physical interpretation remains limited. Nevertheless, CPE behaviour has previously been attributed to adsorption of trace impurities [21], an inherent property of the double-layer charging [22,23], or capacitive dispersion across the electrode surface [24,25]. For Pt(111), CPE behaviour (as quantified by the CPE exponent, α_{dl}) was found to be more pronounced at low electrolyte concentrations [20,26], and we therefore ascribed it to an inhomogeneous current distribution at the disk electrode [24,27].

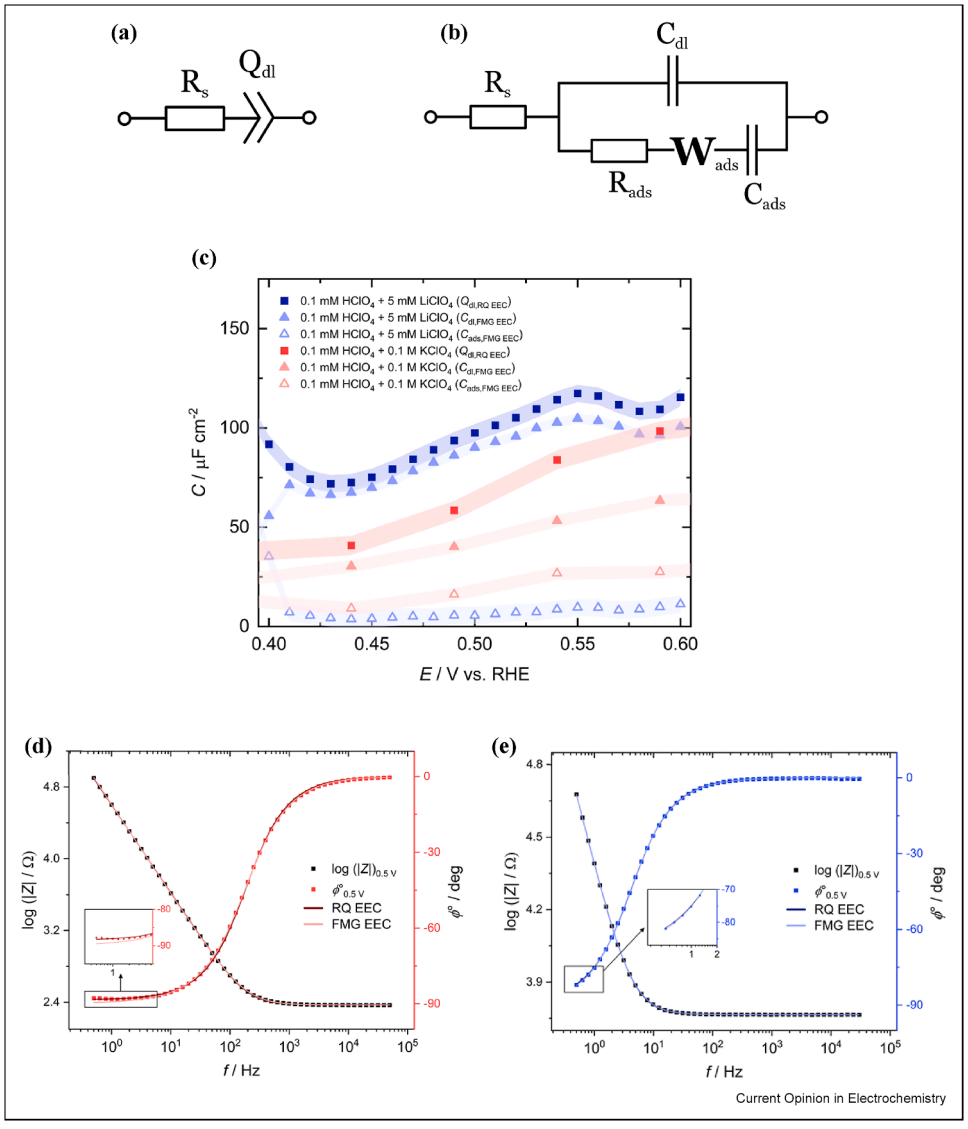
To understand the origin of dispersive capacitance behaviour in a more physical sense, phenomenological models have also been used which are based on continuum-level assumptions. From such an approach, it was concluded that this dispersion is likely attributable to, among other effects such as surface heterogeneity unlikely in the case of single-crystal electrodes [28], a distribution of relaxation times caused by inhomogeneous transport of ions through the double-layer. Kant et al. demonstrated this by linearising the Debye−Falkenhagen equation to describe the potential of an electrode, revealing a close agreement with the capacitance dispersion previously observed on a Au(111) electrode in 0.1 M $HClO_4$ with $\alpha = 0.997$ throughout a frequency regime similar to that presented here [29−31]. However, although such a phenomenological approach does allow for a more tangible understanding of such capacitance dispersion, fitting the EIS response with an EEC including a CPE ultimately allows for an accurate picture of the extent of capacitance dispersion [30], albeit that its origin remains relatively unknown. Therefore, such an empirical approach was deemed appropriate in this case for fitting the EIS response and is used for the rest of the discussion presented in this paper.

Regardless of its origin, CPE behaviour is readily concluded from EIS, whereas from CV, this requires scan-rate−dependent measurements [32]. Still, we showed that the resulting discrepancy in C_{dl} values between the two techniques remains relatively small (∼5 μF cm^{-2}) because α_{dl} remains greater than ∼0.95 even at extremely low electrolyte concentrations (*i.e.* 0.1 mM $HClO_4$) [20]. Therefore, while CPE behaviour is non-negligible, it is insufficient to account for the anomalous trends in the C_{dl} values obtained for the different electrolyte conditions highlighted by Huang et al. (Pt(111) in 0.1 mM $HClO_4$ + 0.1 M $KClO_4$/5 mM $LiClO_4$), which would require a ∼100-μF cm^{-2} difference between EIS and CV [2,13,15]. To verify this point, we repeated the measurements made in these electrolyte conditions using EIS, as shown in Figure 1c−e.

At this point, it is important to emphasise that the choice of EEC is critical to obtaining meaningful C_{dl} values from impedance data. The Nyquist impedance plots (shown in SI Figure 2) at 0.5 V_{RHE} for Pt(111) in 0.1 mM $HClO_4$ + 0.1 M $KClO_4$ and in 0.1 mM $HClO_4$ + 5 mM $LiClO_4$ display, as is expected for the double-layer window, essentially purely capacitive behaviour; that is, no semicircle indicative of charge-transfer resistance associated with adsorption appears in the high-frequency limit (50 kHz). We argue that any deviation from ideal charging behaviour is attributable to CPE behaviour, suggesting that a serial RQ EEC is most appropriate.

However, Pajkossy and Kolb used the Frumkin-Melik-Gaikazyan (FMG) EEC (Figure 1b) to model the impedance response for the double-layer region of Pt (111) in 0.1 mM $HClO_4$ + 0.1 M $KClO_4$ [2]. The FMG circuit models EDL charging in the presence of chemisorption by connecting C_{dl} in parallel with elements

Figure 1



(a) Electrical equivalent circuit (EEC) consisting of a resistor (R_s, solution resistance) connected in series with a constant phase element (CPE, Q_{dl}); **(b)** Frumkin-Melik-Gaikazyan (FMG) EEC where C_{dl} is connected in parallel with elements accounting for chemisorption (serial connection of a resistor, R_{ads}, capacitor, C_{ads}, and Warburg element, W_{ads}, modelling the charge-transfer resistance, pseudo(adsorption)capacitance and diffusion impedance, respectively) [33]; **(c)** Q_{dl} and C_{dl}/C_{ads} values extracted from fitting electrochemical impedance spectroscopy (EIS) data of Pt(111) in 0.1 mM $HClO_4$ + 5 mM $LiClO_4$ and 0.1 mM $HClO_4$ + 0.1 M $KClO_4$ using an EEC consisting of a resistor and CPE connected in series (RQ EEC) and FMG EEC, respectively (ΔE = 10 mV, 50 kHz–0.5 Hz, see SI Figure 1 for CPE exponent (α_{dl}) values for serial RQ EEC fit; Bode impedance plots of Pt(111) in **(d)** 0.1 mM $HClO_4$ + 0.1 M $KClO_4$ and **(e)** 0.1 mM $HClO_4$ + 5 mM $LiClO_4$ at 0.5 V (squares represent raw data) with serial RQ and FMG EEC fits shown overlayed, respectively. Error bars (shown as shaded region) calculated according to SI Section 1.3.

accounting for chemisorption including a capacitor accounting for pseudo(adsorption) capacitance, C_{ads} [34]. Using this EEC, we obtain reasonable C_{dl} values (30–55 μF cm^{-2}, Figure 1c). However, we obtained nonzero C_{ads} values throughout the double-layer region (Figure 1c), which contradicts the common belief that there is no specific adsorption in this potential window and therefore suggests that this may not be the most appropriate EEC in this context [4].

Therefore, we fitted the same EIS data for both electrolytes (0.1 mM $HClO_4$ + 0.1 M $KClO_4$/5 mM $LiClO_4$) with both the serial RQ and FMG EECs, respectively. The serial RQ EEC provided a better fit of the experimental data than the FMG EEC for both electrolytes, particularly in the low-frequency regime (<10 Hz), as shown in the corresponding Bode plots (Figure 1d/e). Furthermore, the Q_{dl} values extracted from fitting with the RQ EEC (35–100 μF cm^{-2}, Figure 1c) are

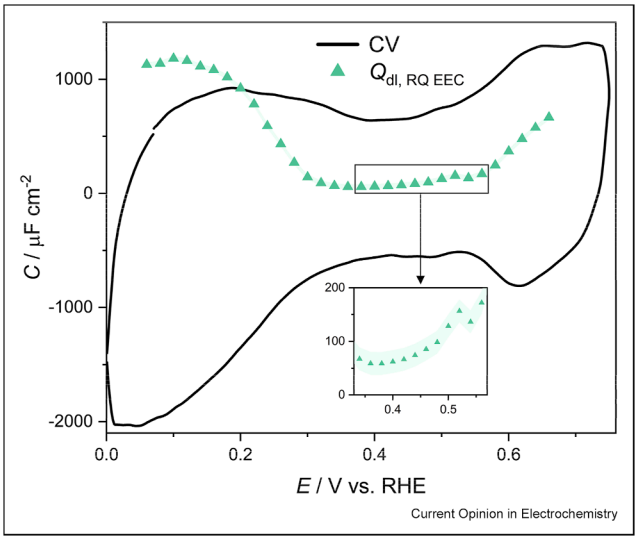
significantly larger than the C_{dl} values (25–50 μF cm^{-2}, Figure 1c) obtained using the FMG EEC. This discrepancy underscores the marked dependence of the obtained double-layer capacitance value on EEC choice and highlights the danger EIS can present in terms of overfitting and data interpretation (see SI Note 2.1).

Nevertheless, comparing the double-layer capacitance values obtained using EIS for Pt(111) measured in 0.1 mM $HClO_4$ + 5 mM $LiClO_4$ with those in 0.1 mM $HClO_4$ + 0.1 M $KClO_4$ confirms the discrepancy noted by Zhang and Huang (SI Figure 3) [13]. Despite the higher bulk ion concentration in the latter electrolyte, $C(Q)_{dl}$ is consistently lower by ∼50(25) μF cm^{-2} (s$^{\alpha-1}$), regardless of the EEC used (Figure 1c). This deviation from the GC theory suggests that the unexpected double-layer capacitance trends cannot be attributed to measurement technique but rather highlights the anomalous nature of the EDL structure at the Pt(111)/aqueous interface [13,16]. As discussed in the introduction, the physical interpretation of these capacitance values are out of the scope of this article, but the reader is referred to other literature [12,14].

A second important experimental issue to consider in the measurement of $C(Q)_{dl}$ of platinum electrodes is the choice of the electrolyte pH. First of all, if it is important to include the PZC in the double-layer window of Pt (111), it is imperative to work in the limited pH range between ∼2 and ∼5 (where only pH 4 actually gives a GC-predicted capacitance minimum at the PZC) [1]. Secondly, in the experimental literature, neutral pH is often chosen for double-layer measurements of platinum and cited in comparison to other measurements or computational data. Neutral pH is logical for electrodes with a wide double-layer potential window (such as Au or Hg) but problematic for Pt electrodes as the narrow, 200-mV wide, double-layer window of Pt (111) is bound by proton-consuming/-generating reactions [4]. Under these conditions, interfacial pH swings are very difficult to avoid using potentiodynamic techniques [35]. To highlight this and to compare to recent literature, we measured Pt(111) in 0.05 M $LiClO_4$ (pH 6) using CV and EIS (Figure 2) [36].

An extreme discrepancy in the $C(Q)_{dl}$ values obtained between CV and EIS can be observed in Figure 2. EIS provides reasonable values of Q_{dl} of ∼50–150 μF cm^{-2} s$^{\alpha-1}$ (0.40–0.55 V) similar to those obtained previously for the same electrolyte conditions [36]. However, the C_{dl} values obtained using CV are anomalously large (∼650 μF cm^{-2}), likely attributable to pH swings exacerbated by potentiodynamic scanning in near-neutral electrolytes. A similar artefact due to local pH swings would be expected for ac voltammetry experiments, although mitigated to some extent by using smaller-potential perturbations [20]. As a result of this pH swing effect and the extreme discrepancy in the C

Figure 2



Pt(111) measured in 0.05 M $LiClO_4$ (pH = 6) using cyclic voltammetry, CV (scan rate = 10 mV s^{-1}) and electrochemical impedance spectroscopy, EIS (ΔE = 10 mV, 30 kHz–1 Hz, fitted with a serial electrical equivalent circuit consisting of a resistor and constant phase element, RQ EEC). See SI Figure 4 for EIS values obtained using the Frumkin-Melik-Gaikazyan EEC and a more in-depth discussion. Error bars (shown as shaded region) calculated according to SI Section 1.3.

$(Q)_{dl}$ values obtained using CV and EIS, it is likely that the accurate determination of such a capacitance value in (near-)neutral conditions using experimental techniques is challenging and highly nontrivial. Therefore, these measurements should not be relied upon for computational/theoretical modelling purposes.

Measurement of C_{dl} in the presence of chemisorption

It is clear that obtaining C_{dl} in the double-layer window of the seemingly simple Pt(111)/$HClO_4$ interface involves inherent complexities despite representing an 'ideal' case in Pt electrochemistry. However, understanding how C_{dl} changes in the presence of chemisorbates is of crucial importance for understanding Pt surfaces under more catalytically relevant conditions.

As mentioned previously, the double-layer window of Pt (111) is bordered by regions where H_{ads} or OH_{ads} exist on the surface. Deconvoluting the adsorption (pseudo) capacitance of H_{ads} and/or OH_{ads} from C_{dl} for the Pt (111)/$HClO_4$ interface is challenging due to the rapid kinetics of adsorption (*i.e.* the RC time of charge-transfer resistance and the adsorption capacitance is typically much smaller than that of the solution resistance and double-layer capacitance) [13,18,37]. However, in alkaline media, the sluggish kinetics of H_{ads} formation from H_2O facilitates the separation of C_{dl} and

C_{ads} using EIS in a standard electrochemical setup. Schouten et al. demonstrated this for Pt(111) in 0.05 M NaOH, where C_{dl} values of ∼10−30 μF cm^{-2} were obtained between 0.05 and 0.80 V_{RHE} using the adsorption EEC proposed by Conway et al. (equivalent to the FMG EEC shown in Figure 1b but without the Warburg element) [18,38]. Notably, smaller C_{dl} values were obtained in the H_{upd} region (0.05−0.40 V_{RHE}) than in the double-layer window (0.40−0.60 V_{RHE}), highlighting the distinct effect of chemisorption on C_{dl}.

In acidic media, however, the kinetics of H_{ads} are much faster (estimated ∼1 MHz in 0.5 M $HClO_4$) [17,37]. Experimentally, measuring at such high frequencies necessitates specialised electrolyte conditions/experimental setups to deconvolute C_{ads} from C_{dl}, due to the presence of a so-called high-frequency artefact related to the slow response of the potentiostats to the frequency perturbation [37,39−41]. Increasing the concentration of the supporting electrolyte can raise the measurable upper-frequency limit to a certain extent as the solution resistance dictates the RC time of the capacitive branch [41]. This was exploited in the work of Pajkossy and Kolb, where they showed that, for sufficiently low proton concentrations (0.1 mM $HClO_4$) with high supporting electrolyte concentrations (0.1 M $KClO_4$), the diffusion of H_3O^+ becomes rate limiting for adsorption such that the H_{ads} process can be deconvoluted from C_{dl} on Pt(111) using the FMG EEC (Figure 3a) [2,33,42].

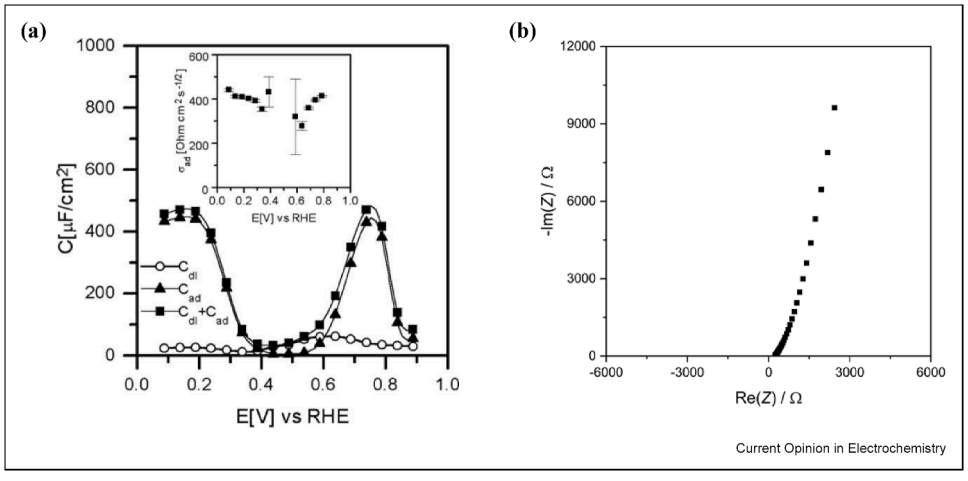
We repeated these EIS measurements in the same electrolyte conditions (0.1 mM $HClO_4$ + 0.1 M $KClO_4$) and confirmed that the impedance response in the H_{upd} region displays two distinct capacitive processes occurring on different timescales (0.09 V_{RHE}, Figure 3b), a phenomenon not observed in the double-layer window (SI Figure 2). Therefore, in this context, the FMG EEC is more appropriate, and a close agreement with the C_{dl} values previously obtained by Pajkossy and Kolb in the H_{upd} region (∼25 μF cm^{-2}, SI Figure 5a) was observed [2,33]. Importantly, however, we find that using an FMG EEC without R_{ct} element (*i.e.* Figure 1b without R_{ads}) to fit the same EIS data results in identical values for C_{dl}, C_{ads}, and W_{ads} (see SI Figures 6 and 7 for comparative fits and obtained values using the FMG EEC with/without R_{ads}, respectively) obtained when using the complete FMG EEC as the R_{ct} values we obtain are extremely small (<1 mΩ cm^2, SI Figure 5b). Therefore, this suggests that the diffusion of the H_3O^+ is indeed rate-limiting to adsorption but that the adsorption of the hydrogen remains too fast to measure [37,42].

However, in 'standard' acidic electrolytes, such as higher-concentration $HClO_4$ or H_2SO_4, no such diffusion limitations exist. To overcome the high-frequency limitations of most potentiostats, Sibert et al. designed a specialised two-electrode setup that enabled measurements up to 1 MHz. This setup allowed C_{dl} (∼35 μF cm^{-2}) to be measured separately from H_{ads} in the H_{upd} region (at 0.16 V_{RHE}) in 0.5 M $HClO_4$ [37]. However, their reported C_{dl} values in the OH_{ads} region were abnormally large (160 μF cm^{-2} at 0.76 V_{RHE}), indicating that the rate of OH_{ads} formation kinetics still poses a technical challenge for adequate deconvolution, even in specialised high-frequency setups [18,37,43,44].

Measurement of C_{dl} on stepped platinum electrodes

Even with chemisorption, Pt(111) is hardly representative of electrocatalytically relevant polycrystalline/

Figure 3



(a) Double-layer capacitance, C_{dl}, and adsorption capacitance, C_{ads}, extracted from a Frumkin-Melik-Gaikazyan electrical equivalent circuit for Pt(111) as measured by Pajkossy and Kolb in 0.1 mM $HClO_4$ + 0.1 M $KClO_4$ between 0.09 and 0.89 V (inset: Warburg coefficient) [2]; **(b)** Nyquist impedance plot of Pt(111) at 0.09 V_{RHE}, ΔE = 10 mV, measured in 0.1 mM $HClO_4$ + 0.1 M $KClO_4$ (50 kHz−0.5 Hz).

nanocrystalline electrodes, which contain defects, step sites, and grain boundaries. It is well established that lower-coordinated Pt facets (*i.e.* (110) and (100)) exhibit a higher propensity for H_2O dissociation, such that as hydrogen is de(ad)sorbed from the surface, hydroxyl species will be concurrently ad(de)sorbed. As a result, any Pt surface, other than Pt(111), will always have some coverage of H_{ads} and/or OH_{ads} in varying ratios at any given potential [6–8,45]. The pseudocapacitance associated with this adsorption is complex and leads to significant ambiguity in interpreting the corresponding capacitance values [5].

We have recently systematically measured and analysed the capacitance of single-crystal Pt(S)-[(n-1)(111)x(110)] and Pt(S)-[n(111)x(100)] electrodes in the double-layer window (0.40–0.60 V_{RHE}) [46]. Specifically, we hypothesise that the OH_{ads} coverage remains constant throughout this window for (110) steps but varies with potential for (100) steps, leading to a significant additional pseudocapacitance measurable in the latter case only. This suggests that the pseudocapacitance associated with the (100) facet will likely dominate the total capacitance measured in the double-layer window of polycrystalline/nanocrystalline Pt electrodes.

The presence of adsorbates and their associated pseudocapacitance has important ramifications for the interpretation of the potential of the capacitance minimum in the 'double-layer' window of platinum electrodes. While the GC theory predicts a capacitance minimum at the PZC in the absence of specific adsorption [47,48], a capacitance minimum observed in the double-layer window does not automatically correspond to the PZC. On Pt electrodes, a GC-like capacitance minimum can only be observed on Pt (111) in extremely dilute 0.1 mM $HClO_4$ electrolyte [1,15]. Nonetheless, an apparent capacitance minimum is nearly always also observable in the 'double-layer' window of other platinum surfaces, such as stepped single-crystalline, or polycrystalline/nanocrystalline platinum electrodes, because the region is bordered by two pseudocapacitive regions with high capacitance. These minima are often mistakenly attributed to the PZC. In reality, no adsorbate-free potential window exists for these surfaces and no PZC can be (easily) obtained from capacitance measurements [6,36,49]. Interestingly, a recent optical method introduced by Suntivich et al. can measure the local interfacial electric field and can therefore identify a PZC of a polycrystalline surface [50]. The value obtained by their method (0.23 V_{SHE}) is slightly lower than that of Pt(111) but agrees well with that of a stepped surface with (111) terraces of a few atoms wide. In fact, considering the pseudocapacitive nature of all Pt facets other than (111), it is likely that the measured PZC of a polycrystalline surface is close to that of small (111) facets.

Conclusion

We have highlighted here the challenges in accurately measuring and interpreting the double-layer capacitance values for the Pt/$HClO_4$ interface. There are several specific conclusions:

1. Pt(111) exhibits frequency dispersion in the EDL region, likely due to nonideal charging and inhomogeneous current distribution rather than (a low level of) specific adsorption.
2. Anomalous differences in C_{dl} values reported in literature are real and not due to measurement methods (*i.e.* CV vs. EIS), although their exact origin remains unclear.
3. Capacitance measurements of platinum at (near-) neutral pH are uncertain in their interpretation as meaningful double-layer capacitances. They are therefore not suitable for comparison to theory.
4. EIS can only separate adsorption (pseudo)capacitance associated with H_{ads} in the H_{upd} region of Pt (111) in alkaline media; OH_{ads} kinetics are too fast to be separated from C_{dl} in all electrolyte conditions.
5. The Pt(100) facet contributes significant pseudocapacitance in the double-layer window, likely dominating the capacitance measured in this window for polycrystalline/nanocrystalline Pt surfaces.
6. A capacitance minimum observed on a Pt electrode, other than for Pt(111) at pH = 4, typically does not represent the PZC. The PZC is masked by pseudocapacitive contributions and an anomalous GC capacitance.

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.

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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.2025.101727.

Data availability

Data will be made available on request.

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