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Double layer of platinum electrodes: Non-monotonic surface charging phenomena and negative double layer capacitance

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In this study, a refined double layer model of platinum electrodes accounting for chemisorbed oxygen species, oriented interfacial water molecules, and ion size effects in solution is presented. It results in a non-monotonic surface charging relation and a peculiar capacitance vs. potential curve with a maximum and possibly negative values in the potential regime of oxide-formation. Published by AIP Publishing. https://doi.org/10.1063/1.5010999

INTRODUCTION

The surface charging relation of a metal electrode is of paramount importance in electrochemistry.\textsuperscript{1,2} It dictates electrostatic interactions between the charged interface and ions in solution and thus governs local reaction conditions at the reaction plane. Thereby, the surface charging relation determines the activity and stability of the electrochemical interface. Historically, the potential of zero charge (pzc), coined by Frumkin\textsuperscript{3} and termed as one of the most fundamental ideas in electrochemistry,\textsuperscript{2} has been employed to describe the surface charging relation,\textsuperscript{4,5} which is usually written as

\[ \sigma^M = C_{dl} (\phi^M - \phi_{pzc}). \]  

In Eq. (1), the double-layer capacitance \( C_{dl} \) is normally considered to be positive-defined and a weakly dependent function of the electrode potential, \( \phi^M \), resulting in a monotonic relation between \( \sigma^M \) and \( \phi^M \).

However, for a Pt electrode, classical radiotracer experiments of Frumkin and Petrii\textsuperscript{6} and more recent laser-pulsed experiments of Garcia-Araez et al.\textsuperscript{7} have revealed a peculiar non-monotonic charging behaviour with consecutive transitions from negative to positive and further to negative surface charge density as \( \phi^M \) is increased from the hydrogen adsorption region to the region of surface oxide formation. This alternating charging behaviour implies that the pzc is an oversimplified concept to describe metal surface charging phenomena in a wide potential range. Therefore, we must go beyond the pzc concept and scrutinize the metal charging relation from first principles.

As discussed in a recent perspective article,\textsuperscript{7} the development of fully fletched density functional theory (DFT)-based methodologies to self-consistently describe electrochemical interfaces will remain a foremost albeit highly ambitious goal in theoretical electrocatalysis for the foreseeable future. In the interim and as the foundation for further computational forays, a viable theoretical methodology of surface charging effects is needed that minimizes the required input from explicit DFT calculations. We have developed and presented a theoretical framework for Pt electrodes that accounts explicitly for the impacts of chemisorbed oxygen species and oriented surficial water molecules.\textsuperscript{8} The model reproduces the negative-positive-negative sequence of transitions in surface charge density. It attributes the negative surface charge density region at high \( \phi^M \) to the surface dipole moment exerted by chemisorbed oxygen that is formed at the Pt surface.

The previous model employed the classical Poisson-Boltzmann (PB) equation of point ions to account for distributions of ions and electrostatic potential in solution.\textsuperscript{8} However, the simple PB equation becomes inadequate to describe the electrified interface at high surface charge density or in concentrated solution, such as realized in ionic liquids.\textsuperscript{9–12} Therefore, in the present study, we amend the previous model by adopting the modified PB equation, which was introduced by Bikerman\textsuperscript{13} and reformulated thereafter by several authors,\textsuperscript{9–12} to account for the ion size effect. Moreover, the differential double layer capacitance \( C_{dl} \), defined as \( \partial \sigma^M / \partial \phi^M \), is derived and discussed in this study. \( C_{dl} \) can be measured using electrochemical impedance spectroscopy (EIS).\textsuperscript{14–16} For practical uses in porous electrode models, the relation \( C_{dl} = f(\phi^M) \) can be employed to parameterize the charging response of the electrified interfaces. In addition, two key parameters of the previous model are modified based on more recent DFT calculations.

THEORY DEVELOPMENT

The structural model for the Pt-solution interface is schematically illustrated in Fig. 1. It consists of (i) a diffuse layer stretching towards the bulk solution,\textsuperscript{17,18} (ii) an outer Helmholtz plane (OHP), at which the closest counter-ions

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interested readers to our previous work developments of the Pt-solution interface model and refer toodes. In what follows, we present modifications and new tions. Notwithstanding, it warrants a qualitative understanding ena such as the one presented here has its fundamental limita-

The self-consistent theory of charging phenomena at the Pt-solution interface unveils the correlation between proper-

Admittedly a mean-field treatment of nanoscale phenomenas such as the one presented here has its fundamental limitations. Notwithstanding, it warrants a qualitative understanding of the complex surface charging behaviour at platinum electrodes. In what follows, we present modifications and new developments of the Pt-solution interface model and refer interested readers to our previous work for further details not re-iterated in this article.

On the solution side, the distribution of dimensionless potential, \( \delta^S = (\phi^S - \phi_{\text{bulk}}^S) / F/RT \), is described by the modified PB equation,

\[
\frac{\partial^2 \delta^S}{\partial \bar{x}^2} = \frac{\sinh \left( \frac{\delta^S}{2} \right)}{1 + 2\gamma \sinh^2 \left( \frac{\delta^S}{2} \right)},
\]

where \( \gamma = 2c_{\text{tot}}/c_{\text{max}} \) with \( c_{\text{max}} \) being the maximal possible local concentration of ions (both cations and anions) is termed as the compacity, \( \bar{x} = x / \lambda_D \) is the dimensionless coordinate with \( \lambda_D = \sqrt{e^S RT / 2F^2} \), being the Debye length, and \( e^S \) is the dielectric constant of the solution with the gas constant \( R \), the temperature \( T \), the Faraday constant \( F \), and the bulk solution potential \( \phi_{\text{bulk}}^S \). Here, solvent molecules are treated implicitly by way of a primitive continuum dielectric model with \( \epsilon^S \). Equation (2) is reduced to the simple PB equation when \( \gamma = 0 \), that is, in the infinitely dilute case.

The boundary conditions to close Eq. (2) are as follows: (i) at the OHP, \( \bar{x} = 0 \),

\[
\nabla \delta^S = -\sigma^M,
\]

where \( \sigma^M = F \lambda_D \sigma^M / RT \epsilon^S \) is the dimensionless surface free charge density, and (ii) in the bulk solution phase at infinite distance, \( \bar{x} = \infty \),

\[
\nabla \delta^S = 0, \quad \delta^S = 0.
\]

Solving Eq. (2) leads to the expression for potential at the OHP, \( \phi_{\text{OHP}} \),

\[
\phi_{\text{OHP}} = \frac{RT}{F} \times \arcsinh \sqrt{\frac{\exp \left( \frac{\delta^M}{2} \right) - 1}{2\gamma}},
\]

where sign \( (\delta^M) = 1 \) for \( \delta^M > 0 \) and sign \( (\delta^M) = -1 \) for \( \delta^M < 0 \).

On the other hand, \( \phi_{\text{OHP}} \) can be calculated from the metal side,

\[
\phi_{\text{OHP}} = \phi^M - \Delta \phi^M - \frac{\mu_{\text{PO}}} {\epsilon_{\text{PO}}} + \frac{N_{\text{tot}} \mu_{\text{w}}}{\epsilon_{\text{IHP}}} \tanh (X) - \sigma^M \left( \frac{\delta_{\text{OHP}}}{\epsilon_{\text{PO}}} + \frac{\delta_{\text{IHP}}}{\epsilon_{\text{IHP}}} \right),
\]

where \( \Delta \phi^M \) is the constant potential drop at the metal surface due to electron spillover, \( \epsilon_{\text{PO}} \) is the dielectric constant of the oxide layer, \( \mu_{\text{w}} \) is the water dipole moment, \( \delta_{\text{OHP}} \) is the thickness of the OHP, \( \epsilon_{\text{IHP}} \) is the dielectric constant of the OHP, \( \delta_{\text{IHP}} \) is the thickness of the IHP, \( \epsilon_{\text{IHP}} \) is the dielectric constant of the IHP.

The effective surficial oxide dipole moment \( \mu_{\text{PO}} \) is approximated by a linear relation,

\[
\mu_{\text{PO}} = N_{\text{tot}} (\theta_{\text{OX}} \varsigma e^\delta_{\text{PO}}) \tag{7}
\]

with \( N_{\text{tot}} \) being the surface atom density, \( \varsigma \) the average charge number of Pt and \( O_{\text{ad}} / O_{\text{ad}} \) atoms, which can be determined from DFT, \( \delta_{\text{OHP}} \) and \( \theta_{\text{OX}} \) the normalized coverage of chemisorbed oxygen species, which is a function of \( \phi^M \) and \( \text{pH} \), as expressed in Eq. (5) of Ref. 8.

The variable \( X \) represents the dimensionless total field-dependent adsorption energy of interfacial water molecules, which is found from the following relation:

\[
\frac{0.6}{\pi \delta_{\text{IHP}}^2} + N_{\text{tot}} \frac{N_A \mu_{\text{w}}^2}{\delta_{\text{IHP}} \epsilon_{\text{IHP}} RT} \tanh (X) - X = \frac{N_A \mu_{\text{w}} \sigma^M}{\epsilon_{\text{IHP}} RT},
\]

with Avogadro number \( N_A \).
combining eqs. (5) and (6) leads to a novel metal charging relation derived from the refined structural model of the Pt-solution interface,
\[
\text{sign}(\dot{\phi}^M) \frac{2RT}{F} \text{arsinh} \left( \sqrt{\frac{1}{2\gamma}} \left( \exp \left( \frac{\gamma}{2} (\dot{\phi}^M)^2 \right) - 1 \right) \right) \\
+ \sigma^M \left( \frac{\delta_{\text{OHIP}}}{\epsilon_{\text{OHIP}}} + \frac{\delta_{\text{IHP}}}{\epsilon_{\text{IHP}}} \right) \\
= \left( \phi^M - \phi^S_{\text{bulk}} \right) - \Delta \phi^M - \frac{\mu_{\text{PO}}}{\epsilon_{\text{OHIP}}} + \frac{N_{\text{tot}}\mu_w}{\epsilon_{\text{IHP}}} \tanh(\chi). \quad (9)
\]

equation (9) reduces to
\[
\text{sign}(\dot{\phi}^M) \frac{2RT}{F} \text{arsinh} \left( \frac{F \lambda_{\text{D}} \sigma^M}{2RT \epsilon^3} \right) + \sigma^M \left( \frac{\delta_{\text{OHIP}}}{\epsilon_{\text{OHIP}}} + \frac{\delta_{\text{IHP}}}{\epsilon_{\text{IHP}}} \right) \\
= \left( \phi^M - \phi^S_{\text{bulk}} \right) - \Delta \phi^M - \frac{\mu_{\text{PO}}}{\epsilon_{\text{OHIP}}} + \frac{N_{\text{tot}}\mu_w}{\epsilon_{\text{IHP}}} \tanh(\chi), \quad (10)
\]

for \(\gamma \to 0\) corresponding to the case of an infinitely dilute solution. surface charging relations derived from the Bockris and Gouy-Chapman-Stern (GCS) models are given in the Appendix. Note that both Bockris and GCS models are modified by taking into account the ion size effect in this paper.

Using \(C_{\text{dl}} = \partial \sigma^M/\partial \phi^M\), an expression for the double layer capacitance can be deduced, which is given by
\[
C_{\text{dl}} = C_{\text{dl}}^{\text{Bockris}} \left( 1 - \chi_{\text{OX}} \right), \quad (11)
\]

Where \(\chi_{\text{OX}}\) is a coefficient accounting for the effect of chemisorbed oxygen species formation on \(C_{\text{dl}}\).

\[
\chi_{\text{OX}} = \frac{N_{\text{tot}}\xi_{\text{PO}} \delta_{\text{PO}}}{\epsilon_{\text{PO}}} \frac{F \theta_{\text{OX}}(1 - \theta_{\text{OX}})}{RT + \xi_{\text{OX}} \theta_{\text{OX}} (1 - \theta_{\text{OX}})}, \quad (12)
\]

with \(\xi_{\text{OX}}\) being the lateral interaction coefficient in the Langmuir adsorption isotherm. Equation (11) indicates that \(C_{\text{dl}}\) is negative when \(\chi_{\text{OX}} > 1\).

\[
C_{\text{dl}}^{\text{Bockris}} = \frac{1}{C_{\text{dl}}^{\text{GCS}}} + \frac{1}{C_{\text{wd}}}. \quad (13)
\]

Here, \(C_{\text{wd}}\) is the capacitance of the water dipole layer,

\[
C_{\text{wd}} = - \left( \frac{0.6}{\pi \delta_{\text{IHP}} N_{\text{tot}}} + 1 \right) \frac{\epsilon_{\text{IHP}}}{\delta_{\text{IHP}}} + \frac{\epsilon_{\text{OHIP}}^2 RT}{N_{\text{A}} N_{\text{tot}} \mu_w^2} \cosh^2(X), \quad (14)
\]

and \(C_{\text{dl}}^{\text{GCS}}\) is the double layer capacitance of the modified GCS model accounting for ion-size effect,

\[
\frac{1}{C_{\text{dl}}^{\text{GCS}}} = \frac{1}{C_{\text{str}}} + \frac{J_D}{\epsilon^3} \left[ \frac{|\dot{\phi}^M| \exp \left( \frac{\gamma (\dot{\phi}^M)^2}{2} \right)}{\sqrt{\frac{1}{2\gamma} \left( \exp \left( \frac{\gamma (\dot{\phi}^M)^2}{2} \right) - 1 \right) + 1}} \times \left( \frac{2}{\gamma} \left( \exp \left( \frac{\gamma (\dot{\phi}^M)^2}{2} \right) - 1 \right) \right)^{-\frac{1}{2}} \right] \quad (15)
\]

**Table I. Model parameters.**

<table>
<thead>
<tr>
<th>Category</th>
<th>Item</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Constant</strong></td>
<td>Gas constant, (R)</td>
<td>8.314 J K(^{-1}) mol(^{-1})</td>
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<tr>
<td></td>
<td>Faraday constant, (F)</td>
<td>96485 C mol(^{-1})</td>
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<td></td>
<td>Temperature, (T)</td>
<td>298.15 K</td>
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<td></td>
<td>Elementary charge, (e)</td>
<td>1.602 176 62 \times 10(^{19}) C</td>
</tr>
<tr>
<td></td>
<td>Avogadro’s number, (N_{\text{A}})</td>
<td>6.02 \times 10(^{23}) mol(^{-1})</td>
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<td></td>
<td>Water dipole moment, (\mu_w)</td>
<td>3.1 D</td>
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<td></td>
<td>Dissociation constant of water, (K_w)</td>
<td>1 \times 10(^{-5}) mol(^{-1}) cm(^{3})</td>
</tr>
<tr>
<td></td>
<td>Concentration of liquid water, (c_l)</td>
<td>5.5 \times 10(^{3}) mol m(^{-3})</td>
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<tr>
<td></td>
<td>Pt atom density, (N_{\text{tot}})</td>
<td>1.5 \times 10(^{19}) mol(^{-3})</td>
</tr>
<tr>
<td></td>
<td>Vacuum permittivity, (\epsilon_0)</td>
<td>8.85 \times 10(^{11}) F m(^{-1})</td>
</tr>
<tr>
<td><strong>Hydrogen adsorption and oxide formation</strong></td>
<td>Equilibrium potential of hydrogen adsorption, (E_{\text{H}}^{0})</td>
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</tr>
<tr>
<td></td>
<td>Lateral interaction parameter of H adsorption, (\xi_{\text{H}}^{0})</td>
<td>29.2 kJ mol(^{-1})</td>
</tr>
<tr>
<td></td>
<td>Index of Pt oxidation mechanism, (v)</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>Equilibrium potential of Pt oxidation, (E_{\text{OX}}^{0})</td>
<td>0.716 V</td>
</tr>
<tr>
<td></td>
<td>Lateral interaction parameter of oxide adsorption, (\xi_{\text{OX}})</td>
<td>64.2(1-(\delta_{\text{OX}})) kJ mol(^{-1})</td>
</tr>
<tr>
<td><strong>Parameters of the interface</strong></td>
<td>Permittivity of the oxide layer, (\epsilon_{\text{PO}})</td>
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</tr>
<tr>
<td></td>
<td>Permittivity of the IHP, (\epsilon_{\text{IHP}})</td>
<td>6 (\epsilon_0)</td>
</tr>
<tr>
<td></td>
<td>Permittivity of the IHP, (\epsilon_{\text{OHIP}})</td>
<td>30 (\epsilon_0)</td>
</tr>
<tr>
<td></td>
<td>Permittivity of bulk water, (\epsilon^3)</td>
<td>78.5 (\epsilon_0)</td>
</tr>
<tr>
<td></td>
<td>Effective thickness of the oxide layer, (\delta_{\text{PO}})</td>
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</tr>
<tr>
<td></td>
<td>Charge number of oxide dipole, (\xi)</td>
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</tr>
<tr>
<td></td>
<td>Thickness of the IHP, (\delta_{\text{IHP}})</td>
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<td></td>
<td>Thickness of the OHIP, (\delta_{\text{OHIP}})</td>
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</tr>
<tr>
<td></td>
<td>Potential drop at Pt surface, (\Delta \phi^M)</td>
<td>0.3 V</td>
</tr>
</tbody>
</table>
FIG. 2. Comparison between the Gouy-Chapman-Stern (GCS) model, the Bockris model, and the refined structural model of electrified interfaces presented in this study, in terms of (a) surface charging relation and (b) double-layer capacitance of a Pt(111) electrode in 0.1M HClO$_4$ at 25 °C. $\gamma = 0$, and other model parameters are given in Table I.

FIG. 3. Ion size effect on the double layer capacitance of a Pt(111) electrode in 0.1M HClO$_4$ at 25 °C calculated using (a) the Bockris model and (b) the presented model.

RESULTS AND DISCUSSION

Model parameters, inherited from our previous study with some modifications, are tabulated in Table I. Figure 2(a) compares surface charging relations of Pt derived from the GCS model, the Bockris model, and the refined structural model presented in this study with $\gamma = 0$. Figure 2(b) shows the differential double-layer capacitance. Both the GCS and Bockris models exhibit an approximately linear charging relation, which can be well described using the classical charging relation based on the pzc concept. The refined structural model of the present study exhibits a non-monotonic charging behaviour with a decrease in $\sigma^M$ at high $\phi^M$, which can be ascribed to the impact of the surface oxide dipoles. This peculiar charging relation is consistent with experiments of Frumkin and Petrii and Garcia-Araez et al. and DFT studies.

Figure 2(b) displays the double-layer capacitance calculated in different models. The double-layer capacitance of the GCS model, $C^{\text{GCS}}$, slightly changes with varying $\phi^M$, and it exhibits the Gouy-Chapman minimum at $\phi^M = \Delta\phi^M$. The double-layer capacitance of the Bockris model, $C^{\text{Bockris}}$, shows a similar behaviour as the GCS model, except that $C^{\text{Bockris}}$ is larger than $C^{\text{GCS}}$, because of the contribution of the ordered water layer. Specifically, at a given $\sigma^M$, the potential difference across the interface in the Bockris model has a smaller magnitude than that in the GCS model due to the buffering effect exerted by interfacial water molecules. Consequently, we find $C^{\text{Bockris}} > C^{\text{GCS}}$. It is noted that the Gouy-Chapman minimum disappears and evolves into a maximum when $\gamma$ increases, as shown in Fig. 3(a) and explored and explained in Ref. 12. $C^{\text{dl}}$ derived with the structural capacitance of the Pt-solution interface defined as

$$\frac{1}{C^{\text{str}}} = \frac{\delta_{\text{OHP}}}{\epsilon_{\text{OHP}}} + \frac{\delta_{\text{IHP}}}{\epsilon_{\text{IHP}}}.$$  (16)

Herein, we assume that the contribution of the chemisorbed oxide to the structural capacitance is minor.

FIG. 4. Comparison between model and experiment in terms of the double-layer capacitance of a Pt(111) electrode in 0.1 mM HClO$_4$ + 0.1M KClO$_4$ at 25 °C. Adjusted model parameters are as follows: $E_{\text{OX}}^0 = 0.8$ V, $\Delta\phi^M = 0.15$ V, and the number of water molecules per Pt site (one for the solid line and ten for the dashed line).
from the refined structural model agrees with \( C_{\text{dl}}^{\text{Bockris}} \) in the low potential range without formation of chemisorbed oxygen species. However, at high potentials, \( C_{\text{dl}} \) decreases relative to \( C_{\text{dl}}^{\text{Bockris}} \) and even assumes negative values when \( \phi^M > 0.7 \) V. \( C_{\text{dl}} \) goes through a maximum at \( \phi^M \sim 0.5 \) V, where \( \phi_{\text{OH}} = 0.05 \) V.

Kornyshev predicted bell- or camel-shaped capacitance-potential curves using a modified PB equation, which is reproduced in Fig. 3(a). Two symmetrical maxima due to the size effect are observed on the bell-shaped curve for a symmetrical electrolyte. However, in our case, the capacitance maximum at \( \phi^M \sim 0.5 \) V in Fig. 2(b) is not caused by the crowding of counterions, as the compacity is \( \gamma = 0 \) in Fig. 2. This peculiar capacitance maximum is ascribed to the surface oxide dipole formed on the Pt surface.

Ion size effects on \( C_{\text{dl}} \) derived from this model are shown in Fig. 3(b). The maximum due to the surface oxide dipole disappears when \( \gamma \) increases to 0.5, implying that it is easier to observe this maximum in dilute solution. In the Kornyshev approach, the capacitance-potential curve of a symmetrical electrolyte preserves symmetry around the pzc. Asymmetry can be introduced by accounting for different sizes and charge numbers of anions and cations. The model presented in this study unravels another kind of asymmetry in the capacitance-potential curve that is caused by asymmetry in the specific adsorption state of the electrode.

Pajkossy and Kolb employed EIS to determine the \( C_{\text{dl}} \) of Pt (111) and Pt (100) electrodes in various 0.1M electrolyte solutions. The measured \( C_{\text{dl}} \) versus \( \phi^M \) curves exhibited a maximum in the potential range of \(-0.5 \) V (SHE) for both electrodes regardless of variations in solute chemistry or solution pH. The authors tentatively correlated the maximum with the pzc and conjectured that Gouy-Chapman theory fails in solutions with concentration exceeding 0.1M. To prove or disprove this hypothesis, they lowered the solution concentration to 1 mM in a subsequent study. At such a low solute concentration, they expected that the \( C_{\text{dl}} \) versus \( \phi^M \) curve would show a Gouy-Chapman minimum. However, the maximum still showed; see Fig. 4. They concluded that this phenomenon cannot be attributed to the pzc, but it might be related to changes in the orientation of water molecules at the Pt-solution interface. However, this explanation is at odds with the Bockris model that considers surficial water molecules but does not produce a capacitance maximum, as seen in Fig. 2(b). Another salient feature is that \( C_{\text{dl}} \) decreases as \( \phi^M \) increases from 0.4 V to 0.6 V (SHE), where the formation of chemisorbed oxygen species progresses, as revealed by Pajkossy and Kolb using the EIS method, and also by Garcia-Araez et al. who developed a thermodynamic approach to determine \( C_{\text{dl}} \). The model presented in this article qualitatively reproduces both features, the capacitance maximum at \(-0.4 \) V and the decreasing trend in \( C_{\text{dl}} \) with increasing \( \phi^M \) in the potential range of 0.4–0.6 V, as shown in Fig. 4. We find that the location of the Gouy-Chapman minimum and the surface-oxide related maximum are dictated by \( \Delta \phi^{\text{M}} \) and \( E_{\text{OX}}^{0} \), which are adjusted to \( E_{\text{OX}}^{0} = 0.8 \) V, \( \Delta \phi^{\text{M}} = 0.15 \) V in Fig. 4, respectively. Noticeable deviation between the model and experiment is found regarding the ratio between the maximum and the minimum. Experimental data show a steeper transition from the minimum to the maximum. Parametric analysis reveals that the buffering effect exerted by interfacial water molecules affects the ratio between the maximum and the minimum in the double-layer capacitance curve. The dashed line corresponding to the case with ten water molecules per Pt sites, namely, a stronger buffering effect, shows a steeper transition. The agreement between model and experiment can be improved by employing an explicit treatment of solvent molecules, as in Ref. 25. We also note that experimental data of double-layer capacitance of Pt are rare in the literature, and there exists a significant variation among different sources.

The partial charge number \( \zeta \) is a key interfacial property that can be determined conveniently by DFT studies. Figure 5(a) indicates that a larger \( \zeta \), namely, a greater surface oxide dipole, decreases \( \sigma^{\text{M}} \) to more negative values in the high potential range, leading to a more negative \( C_{\text{dl}} \). Moreover, the maximum in \( C_{\text{dl}} \) occurs at higher \( \phi^{\text{M}} \) when \( \zeta \) decreases. Figure 5(b) displays the pH effect on \( C_{\text{dl}} \). At higher pH, oxide formation commences at lower potentials, decreasing \( \sigma^{\text{M}} \) to more negative values. Note that the present theory does not treat the phenomenon of oxide growth beyond the monolayer structure and its impact on the metal surface charging phenomenon.

**CONCLUSION**

In summary, a recently presented structural model of electrified interfaces that incorporates the formation of chemisorbed oxygen species and a layer of oriented water molecules has been improved by taking into account ion
size effects. Moreover, an explicit expression for the double layer capacitance has been derived. Compared with the Gouy-Chapman-Stern and Bockris models, the presented model gives rise to a non-monotonic surface charging relation and a peculiar maximum of the double layer capacitance due to Pt surface oxide formation. Recent experimental studies from the Petri group and the Feliu group support the non-monotonic surface charging relation with a second negative region in the high potential range with oxide formation. Parametric analysis reveals that the surface oxide-induced capacitance maximum disappears when the ion size coefficient \( \gamma \) grows as a consequence of the increase in solute concentration.

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APPENDIX: METAL SURFACE CHARGING RELATION OF CONVENTIONAL MODELS AND NOTES ON MODEL PARAMETERS

1. Metal surface charging relation of the Bockris and GCS models

The metal charging relation derived from the Bockris model that does not consider the surface oxide layer is given by

\[
\operatorname{sgn}(\sigma^M) \frac{2RT}{F} \times \arcsinh \left( \frac{1}{2\gamma} \left( \exp \left( \frac{\gamma}{2} (\sigma^M)^2 \right) - 1 \right) \right) + \sigma^M \left( \frac{\delta_{\text{OH}}}{\epsilon_{\text{OH}}} + \frac{\delta_{\text{HP}}}{\epsilon_{\text{HP}}} \right) = \left( \phi^M - \phi_{\text{bulk}}^S \right) - \Delta\phi^M + \frac{N_{\text{tot}} \mu_w}{\epsilon_{\text{HP}}}, \tanh(X) \tag{A1}
\]

and that derived from the GCS model that does not account for neither the surface oxide layer nor the surface water molecule layer is given by

\[
\operatorname{sgn}(\sigma^M) \frac{2RT}{F} \times \arcsinh \left( \frac{1}{2\gamma} \left( \exp \left( \frac{\gamma}{2} (\sigma^M)^2 \right) - 1 \right) \right) + \sigma^M \left( \frac{\delta_{\text{OH}}}{\epsilon_{\text{OH}}} + \frac{\delta_{\text{HP}}}{\epsilon_{\text{HP}}} \right) = \left( \phi^M - \phi_{\text{bulk}}^S \right) - \Delta\phi^M. \tag{A2}
\]

Note that both the Bockris and GCS models have been improved over their original forms by accounting for the ion size effect.

2. Notes on model parameters

In our previous work, we assumed that \( \epsilon_{\text{PTO}} = 30\epsilon_0 \) based on dielectric constants of bulk metal oxides. However, one should note that there is nothing but vacuum between Pt and O\(_{\text{ad}}\) atoms in the monolayer. As a result, \( \epsilon_{\text{PTO}} = 1 \) should be used for the medium between Pt and O\(_{\text{ad}}\) atoms. In addition, we used \( \varsigma = 0.8 \), based on our previous DFT calculation of the surface oxide dipole. However, a more recent comprehensive DFT study of chemisorbed oxygen on Pt(111) shows that the surface oxide dipole is much smaller. As a result, we used a new value of 0.01 in this work.


