Electrochemical characteristics of ideal polarizable interfaces with limited number of charge carriers

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Recent progress in material chemistry and surface engineering has led to emergence of new electrode materials with unique physical and electrochemical properties. Here, we introduce a physical model describing charging of ideal polarizable electrode-electrolyte interface where the electrode is characterized by a limited capacity to store charge. The analytical model treats the electrode and electrolyte phases as independent nonlinear capacitors that are eventually coupled through the condition of equality of the total stored electrolyte are used to predict dependencies of differential capacitance of the electrolyte phase and surface concentration of the electrical charge on the applied potential. The model of the nonlinear capacitor for the electrode phase is described by a theory of electron donors and acceptors present in conductive solids as a result of thermal fluctuations. Both the differential capacitance and the surface concentration of the electrode phase to accumulate charge and its ability to form electron donors and acceptors. The knowledge of capacitive properties of both phases allows to predict electrochemical characteristics of ideal polarizable interfaces, e.g., current responses in linear sweep voltammetry. The coupled model also shows significant potential drops in the electrode comparable to those in the electrolyte phase for materials with low charge carrier concentrations.

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I. INTRODUCTION

Electrochemical characteristics of ideal polarizable interfaces (IPI) bring important information about the dynamics of charging processes and the properties of both phases such as the concentration of electric charge carriers or the composition of electrolytes. Understanding the charging process and interface structure allows better interpretation of experimentally observed electrochemical characteristics such as polarization curves, cyclic voltammograms, or impedance spectra, e.g., Refs. [1,2]. For example, one can differentiate between the faradaic charge transfer through the interface, capacitive, or adsorption processes [3].

In this work, IPI formed by an aqueous electrolyte on one side and another phase on the other side is considered. The nonelectrolyte phase is conductive and can be represented by a metal conductor [4], semimetal [5], semiconductor [6], or doped dielectrics [7]. The nonelectrolyte phase is called the electrode in the following text.

The aforementioned interfaces appear in many modern and traditional applications such as electrochemical microsensing and biosensing [8], photocatalysis [9], nanopore transistors [10], desalination [11], or devices for energy storage and production such as supercapacitors [12], batteries, or fuel cells [13]. IPIs are also exploited in energy efficient operations such as capacitive deionization of water solutions on carbon microporous electrodes [14,15].

When the electrode phase is formed by a thick layer of a metal conductor, there is an abundance of free electrons in this phase. Almost entire drop of electric potential is localized in the aqueous electrolyte and electrochemical measurement reveals only capacitive and resistive properties of the electrolyte. However, the electrode layer can contain limited number of free charge carriers. Typical examples are electrodes made of common semiconductor layers, graphene [16], diamond films [17], or metal coatings formed by a few atomic layers [18]. Capacitive processes within the electrode itself become important and both sides of the interface have to be treated together to predict various electrochemical characteristics.

II. OBJECTIVES

One of the possible models of IPI relied on dividing IPI into three domains where two charged phases are separated by one insulating layer of finite thickness [19,20]. This approach based on statistical mechanics allowed to estimate interfacial properties of IPI (differential capacity, surface tension, or potential drop distribution).

In this work, we treat each side of the IPI as a nonlinear capacitor. The total potential drop across the interface is then divided between these two elements. The knowledge about capacitances of both sides of IPI allows to predict electric current responses to an applied voltage signal.

In the following section, mathematical equations relating the ion concentration, surface electric charge, potential drop in the diffuse part of electric double layer (EDL), and the differential capacitance for 1: n electrolyte are summarized. Classical Gouy-Chapman theory leading to the Poisson-Boltzmann (PB) equation is applicable only for dilute electrolytes and small potential drops [21]. To get characteristics of IPI under higher voltage, we employ the theory describing formation of condensed ionic layers (CL) at charged surfaces [22].

PB and CL models of the diffuse part of EDL have been extensively analyzed for 1 : 1 electrolytes in Ref. [21], where basic properties such as differential and integral capacitances are provided. An important property of the CL model represents a decrease in EDL capacitance if a high voltage is applied on EDL. It can explain observed flow reversals in ac electroosmotic pumps [23]. Understanding of dynamic and near-equilibrium behaviors of EDL at electrode-electrolyte interface is important in applications such as desalination due to capacitive charging [24], faradaic interactions in porous electrodes or metallic foams [25,26], hydrogen fuel cells [27], or thin film electrolytes in batteries [28]. If electrochemical reactions occur in a system, PB or CL models have to be coupled with the description of electrode kinetics typically based on the Butler-Volmer equation or its modifications [29].

In this work, both approaches to the treatment of the diffuse layer based on either the PB equation or the Bikerman equation for the condensed layer are used. We show that the capacitive character of the electrolyte phase strongly depends on the valency of ions dissolved in the electrolyte. In this study, 1:n electrolyte is considered, where the symbol n is the valency of an anion, e.g., n = -1 for potassium chloride or n = -2 for potassium sulfate. The effects of valency on the electric double layer capacitance are often neglected, which, however, may lead to misinterpretation of electrochemical analysis of aqueous electrolytes.

Section IV deals with the capacitive properties of the electrode phase that can be represented by different materials. Electric charge is localized at the electrode surface in the form of electron and/or hole deficiency or excess. The electron concentration in semiconductors is typically $10^{6}-10^{8}$ times lower than that in metal conductors [29]. Therefore, nonzero drop of electric potential develops at the surface layer of the electrode phase. Then, the potential drop is not only a result of electrolyte properties, but also the properties of the electrode phase itself. Possible thermodynamic treatment of the electrode layer has been recently discussed in Ref. [30].

Finally, theoretical current responses of IPI to linear sweep voltammetry at low sweep rates are constructed. As there are no diffusion limitations in such regimes, the charging process of IPI interface can be studied independently of bulk phenomena. The effect of limited number of charge carriers on the potential drop inside the electrode phase is also discussed.

The main results of this work can be summarized as follows: (i) the relationships for differential and integral capacitances of the diffuse part of EDL were derived for 1:*n* electrolyte by means of widely used Poisson-Boltzmann and Bikerman equations, (ii) the capacitance of the charged region of an electrode phase with limited number of charge carriers was derived using a donor-acceptor theory, (iii) our IPI model can predict current responses to a voltage signal in near equilibrium regimes by treating the electrode-electrolyte interface as a system of two capacitors in series, (iv) it is shown that the introduction of the electrode-electrolyte interface even under high voltage.

III. DIFFUSE LAYER

A. Poisson-Boltzmann (PB) model

Electrically charged electrodes attract counterions and repel coions in the adjacent layer of aqueous electrolyte (Fig. 1). As a result, a thin layer of an electrolyte with nonzero net electric charge is formed. This region is called a diffuse part of the electric double layer. Ions are transported by two mechanisms



FIG. 1. Electrode-electrolyte interface.

in the vicinity of electrodes: diffusion and electromigration. In equilibrium, the concentration profile of z_i -valent ion obeys the Boltzmann distribution

$$c_i = c_i^0 \exp[-z_i F \phi/(RT)], \qquad (1)$$

where z_i , F = 96485 C mol⁻¹, R = 8.314 J K⁻¹mol⁻¹, Tare the ion charge number, the Faraday constant, the molar gas constant, and the temperature, respectively. To simplify mathematical expressions in the following text, we introduce thermal voltage defined as $\psi \equiv RT/F \approx 26$ mV. The symbol c_i^0 represents the bulk concentration of the ion. ϕ is a local value of electric potential. The reference zero value of electric potential is chosen in the electrolyte bulk.

The distribution of electric potential in the diffuse layer can be calculated from the Poisson equation. Here, we will assume a spatially one-dimensional system with a constant permittivity and 1: n electrolyte

$$\varepsilon \frac{d^2 \phi}{dx^2} = -F \sum_i z_i c_i = -F(c_1 + nc_n), \qquad (2)$$

where ε is the electrolyte permittivity, c_1 and c_n are the concentrations of a univalent cation and *n*-valent anion, *n* is the anion charge number (negative integer). The following parameter values were used in our study: T = 298 K, $\varepsilon = 7.083 \times 10^{-10}$ F m⁻¹, and $c_n^0 = 500$ mol m⁻³.

The local electroneutrality in the electrolyte bulk is satisfied, i.e.,

$$c_1^0 = |n|c_n^0 \,. \tag{3}$$

By combining Eqs. (1)–(3), we obtain the Poisson-Boltzmann equation for 1:*n* electrolyte:

$$\frac{d^2\phi}{dx^2} = -\frac{2Fc_n^0}{\varepsilon} \bigg[|n| \exp\left(-\frac{\phi}{\psi}\right) + n \exp\left(-\frac{n\phi}{\psi}\right) \bigg].$$
(4)

Multiplying both sides of Eq. (4) by $d\phi/dx$, integrating, and using the boundary condition $x \to \infty$, $\phi \to 0$, $d\phi/dx \to 0$ we obtain

$$\frac{d\phi}{dx} = -\operatorname{sgn}(\phi) \sqrt{2c_n^0 RT \left[e^{-\frac{n\phi}{\psi}} - 1 + |n|(e^{-\frac{\phi}{\psi}} - 1) \right] / \varepsilon}.$$
 (5)

The surface concentration of electric charge on a planar electrode phase σ can be calculated using the Gauss law

$$\sigma = -\varepsilon \frac{d\phi}{dx}\Big|_{x=0}.$$
 (6)



FIG. 2. PB model. Dependencies of the surface concentration of electric charge on the surface potential.

If ϕ_0 is the electric potential on the electrode surface, then the surface electric charge is

$$\sigma = \operatorname{sgn}(\phi_0) \sqrt{2c_n^0 \varepsilon RT \left[e^{-\frac{n\phi_0}{\psi}} - 1 + |n| \left(e^{-\frac{\phi_0}{\psi}} - 1 \right) \right]}.$$
 (7)

One can see that the dependence of σ on the surface electric potential is an odd function only for a symmetric 1:1 electrolyte (Fig. 2). As the valency of the anion increases, the same positive value of the surface electric charge is reached at significantly lower positive potential. This is because the anion concentration at the electrode surface increases according to the Boltzmann distribution $c_n \propto \exp(n\phi_0)$ [Eq. (1)]. At negative potentials, differences among the dependencies plotted in Fig. 2 are relatively small due to the cation distribution $c_1 \propto |n| \exp(\phi_0)$.

To make theoretical predictions on electric current responses in voltammetry measurements, we need to determine the differential capacitance of the diffuse layer C_d :

$$C_{\rm d} \equiv \left. \frac{d\sigma}{d\phi} \right|_{\phi = \phi_0}.\tag{8}$$

The Poisson-Boltzmann model gives

$$C_{\rm d} = {\rm sgn}(\phi_0) \ \sqrt{\frac{\varepsilon c_n^0 F}{2\psi}} \frac{e^{\frac{-(n+1)\phi_0}{\psi}} \left(n e^{\frac{\phi_0}{\psi}} + |n| e^{\frac{n\phi_0}{\psi}}\right)}{\sqrt{e^{\frac{-n\phi_0}{\psi}} + |n| \left(e^{\frac{-\phi_0}{\psi}} - 1\right) - 1}} \ . \tag{9}$$

The differential capacitance for $\phi_0 \rightarrow 0$ is a monotonously increasing function of the anion valency at a constant c_n^0 :

$$\lim_{\phi_0 \to 0} C_{\rm d} = \sqrt{\varepsilon c_n^0 F n(n-1)/\psi} . \tag{10}$$

The dependence of the differential capacitance on ϕ_0 exhibits single minimum which is localized at $\phi_0 = 0$ only for the symmetric 1:1 electrolyte (Fig. 3). The differential capacitance



FIG. 3. PB model. The dependence of the differential capacitance on the surface electrode potential. The filled circles depict the limit capacitance values given by Eq. (10).

of the diffuse layer is sometimes assumed to be independent of voltage for potentials $|\phi_0| \approx \psi$. However, the dependencies plotted in Fig. 3 show that such approximation is not valid even for zero potential.

B. Condensed layer (CL) model

The Poisson-Boltzmann equation gives us useful insight into the behavior of the diffuse layer. However, finite size of hydrated ions limits their maximal possible concentration at the electrode surface. For example, the diameters of hydrated potassium, chloride, sulphate, and phosphate ions are 0.424, 0.448, 0.518, and 0.584 nm, respectively. The diameters of other ions can be found in Ref. [31]. At certain value of ϕ_0 , a condensed layer of counterions is formed at the electrode surface.

Modified distribution of the ion concentrations that takes into account the steric limits originally derived by Bikerman [32] and reported also in [33,34] reads as

$$c_{i} = \frac{1}{N_{a}} \frac{N_{t} N_{i}^{0} / N_{f}^{0} e^{\frac{-z_{i} \phi}{\psi}}}{\left[1 + \sum_{j} N_{j}^{0} / N_{f}^{0} e^{\frac{-z_{j} \phi}{\psi}}\right]}.$$
 (11)

The electrolyte domain is considered to be a spatial lattice with the edge length of *a*. It is assumed that one cubic element a^3 of the lattice can by occupied only by one hydrated ion. The value of the lattice parameter *a* was chosen 0.5 nm in this study. The total volume concentration of lattice elements N_t is conserved and equal to

$$N_{\rm t} = 1/a^3 = \sum_j N_j + N_{\rm f} \,.$$
 (12)

Here, N_j and N_f are the volume concentrations of the lattice elements occupied by the *j*th ion and the lattice elements not occupied by any ion, respectively.

In the bulk of 1:n electrolyte, Eq. (12) can be rewritten using the molar bulk concentrations

$$1/a^{3} = c_{1}^{0}N_{a} + c_{n}^{0}N_{a} + N_{f}^{0} = (1 + |n|)c_{n}^{0}N_{a} + N_{f}^{0}, \quad (13)$$

where the Avogadro number N_a is $6.022 \times 10^{23} \text{ mol}^{-1}$. The superscript 0 again denotes the bulk quantities. The volume fraction of elements occupied by any ion in the bulk is then

$$y = (1 + |n|)c_n^0 N_a a^3.$$
(14)

The concentration distributions of ions given by Eq. (11) can be substituted into Eq. (2). The modified Poisson-Boltzmann equation then reads as

$$\varepsilon \frac{d^2 \phi}{dx^2} = \frac{F c_n^0 (1+|n|) \left[n e^{\frac{\phi}{\psi}} + |n| e^{\frac{n\phi}{\psi}} \right]}{(y-1)(1+|n|) e^{\frac{(1+n)\phi}{\psi}} - y \left[e^{\frac{\phi}{\psi}} + |n| e^{\frac{n\phi}{\psi}} \right]}.$$
 (15)

We can solve Eq. (15) in the same manner as the original Poisson-Boltzmann equation [Eq. (4)] to get the density of the surface electric charge

$$\sigma = \operatorname{sgn}(\phi_0) \sqrt{-2\varepsilon c_n^0 (1+|n|) [F\phi_0(1+n) + RT \ln(A)]/y},$$
(16)

where A is

$$A = \frac{(1+|n|)}{(1-y)(1+|n|)e^{\frac{(1+n)\phi_0}{\psi}} + y\left(e^{\frac{\phi_0}{\psi}} + |n|e^{\frac{n\phi_0}{\psi}}\right)}.$$
 (17)

The corresponding dependencies of the surface electric charge on the surface electrode potential are plotted in Fig. 4. The condensed layer model predicts much smaller



FIG. 4. CL model. Dependencies of the surface concentration of electric charge on the surface potential. The dashed lines represent the predictions of PB model.



FIG. 5. CL model. The dependence of the differential capacitance on the surface electrode potential. The dashed lines represent the predictions of PB model.

concentrations of the electric charge than PB model even for relatively low applied potentials, e.g., the validity of PB model in the case of 1 : -3 electrolyte is significantly violated for $\phi_0 < 50$ mV. Similarly to the PB model predictions, the dependence (16) is monotonously increasing with the surface electrode potential.

The dependence of the differential capacitance on the surface electrode potential (Fig. 5) reads as

$$C_{\rm d} = \frac{-\text{sgn}(\phi_0)\sqrt{c_n^0}FA\left(ne^{\frac{\varphi_0}{\psi}} + |n|e^{\frac{n\varphi_0}{\psi}}\right)}{\sqrt{-2(1+|n|)[F\phi_0(1+n) + RT\ln(A)]/(\varepsilon y)}}.$$
 (18)

The dependencies of the differential capacitance are strongly asymmetric with respect to zero potential for |n| > 1. Ions with higher valency provide higher differential capacitances than univalent ions due to higher charge concentration in the condensed layer. This asymmetry necessarily leads to asymmetric responses of electric current to a linear voltage sweep during capacitive charging of the surface. As a result of the condensed layer formation, the dependencies plotted in Fig. 5 exhibit two maxima and are monotonously decreasing when $|\phi_0|$ exceeds a certain critical value.

In summary, we have introduced basic principles of the Poisson-Boltzmann and condensed layer theories of the diffuse layer and derived mathematical expressions for the differential capacitances of the diffuse layer for 1:*n* aqueous electrolytes.

C. Other models

There are other models of EDL that, e.g., include the formation of the Stern (compact) layer [35] without ion centers directly at the charged surfaces or more sophisticated treatment of the steric effects in the diffuse layer.

The concept of condensed layer which takes steric effect into account has been widely discussed by Kilic *et al.* [21].

In this paper, the authors concluded that a significant fraction of applied voltage has to be sustained in the diffuse layer at larger voltages providing a support for neglecting Stern layer effects. Moreover, we show in Sec. V that the introduction of an electrode layer capacitor leads to effects similar to those predicted by models including the Stern layer. Particularly, infinite increase in differential capacitance given by PB model is eliminated.

It was shown that the predictions of the CL model based on the Bikerman equation (11) are not accurate and they can underestimate the excluded volume in aqueous electrolytes. Further, the model does not take into account possible differences in the size of ions [36]. More precise models built on the Carnahan-Starling equation of state have been developed [37,38] and used to explain processes related to sedimentation [39] or polymer adsorption [40].

Another limitation of the CL model may result from possible crowding and overscreening effects under high voltage as predicted, e.g., in [41]. When the separation distance between two point charges is less than the Bjerrum length $\lambda_{\rm B} = (z_i F)^2 / (4\pi \varepsilon RT N_{\rm a})$, the energy of electrostatic interaction prevails the thermal energy. This can lead to the formation of overscreened or crowded double layers that are characterized by changes of charge polarity across EDL. For example, when the surface electric charge density is 1 C m⁻², about six monovalent ions or two trivalent ions have to be localized in 1 nm². Under the conditions chosen in our study, the Bjerrum length is about 7 and 63 Å for monovalent and trivalent ions, respectively. This suggests that crowded double layers may be formed under voltage less than 100 mV (see Fig. 4).

Other information on properties of electric double layers and/or on alternative description of the electric double layers can be found, e.g., in Refs. [42,43].

IV. ELECTRODE PHASE

A. Structure of electrode-electrolyte interface

To really understand the polarization phenomenon at IPI surfaces, we have to include the charging process inside the electrode phase. The IPI polarization leads to the formation of two separated clouds of electric charge. One of them is localized in the diffuse layer of the EDL and the other one, of the same amount but with opposite charge, within the electrode phase (see Fig. 6). There is no direct electric charge transfer between the two phases at IPI. According to the Gauss law, the electric charge in the electrode phase has to be localized at the surface. The finite thickness of the charged layer inside the electrode is usually estimated as the Thomas-Fermi screening length $\lambda_{\rm F}$, which is about 0.5 Å for copper [44] and about 2.5 Å for germanium [45]. These materials represent conductors and semiconductors, respectively. For the sake of comparison, the Debye length λ_D , i.e., the typical thickness of the diffuse layer, in aqueous electrolytes ranges from ≈ 1 nm to ≈ 100 nm according to the electrolyte ionic strength I. By nondimensionalizing the Poisson-Boltzmann equation [46], we arrive at $\lambda_D \propto 1/\sqrt{I}$. Because $\lambda_F \ll \lambda_D$, one can assume that the electric charge is localized just on the electrode surface. If necessary, expressions for the potential and electric



FIG. 6. Structure of the electrode-electrolyte interface. Electric current flows with the density i through the system during the polarization process. Electric charge emerging on the electrolyte side is balanced with the charge in the electrode phase.

charge distribution inside a semiconductor can be found elsewhere [47–49].

The process of electrode polarization is not limited by the transport of electric charge carries inside the solid phase. The electron mobility in copper is about $4 \times 10^{-3} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$ and the electron/hole mobilities in semiconductors are $\sim 10^{-1} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$ [50]. Typical mobilities of hydrated ions in diluted electrolytes are only $\sim 10^{-7} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$ [51].

The presence of electric charge within the electrode phase is necessarily accompanied by a nonzero drop of electric potential $\phi_P - \phi_0$ that will depend on the concentration of available charge carries in the phase. One can determine concentrations of charge carriers as well as the potential drop in the electrode phase by using a simple model that has been introduced recently [30]. The main features of the model are summarized and discussed in the following section.

B. Concept of electron donors and acceptors

Thermal fluctuations in an electrode matter lead to the formation of small areas either with electron excess (electron donors, D^-) or electron deficiency (electron acceptors, A^+). The formation and recombination of electron donors and acceptors can be written in the form similar to a chemical reaction

$$2S \rightleftharpoons A^+ + D^-. \tag{19}$$

The above equation expresses the fact that thermal fluctuations of charge carriers between two electroneutral pieces of matter S give rise to the formation of electron acceptors and donors.

As the mobilities of charge carriers in the electrode phase are very high, we can assume that the process of formation of electric charge carriers reaches the thermal equilibrium expressed by an equilibrium constant K_s :

$$K_{\rm s} = c_{\rm A^+} c_{\rm D^-} / c_{\rm S}^2, \tag{20}$$

where c_{A^+} , c_{D^-} , and c_S are the surface concentrations of the electron acceptors, electron donors, and remaining electroneutral areas.

The concentrations of the electron mediators are naturally volumetric. Because the electron mediators are localized very close to the solid-electrolyte interface (the Thomas-Fermi screening length in metals is less than 1 Å), one can expect that the electric charge is effectively localized at the surface. In our previous paper [30] we showed that the formulation of the model by means of surface concentrations is thermodynamically consistent when the space charge region is very thin. We emphasize that the electric charge distribution inside the solid phase has to be considered out of this limit.

The appearance of a nonzero electric charge at electrode surface is given by the excess of either donors or acceptors at the solid surface. The surface concentration of electric charge is

$$\sigma = F(c_{A^+} - c_{D^-}). \tag{21}$$

Finally, the total concentration of elements in the solid c_{tot} that can behave as either electron donors or acceptors is finite and conserved

$$c_{\rm tot} = c_{\rm A^+} + c_{\rm D^-} + c_{\rm S}.$$
 (22)

The equality of electrochemical potentials in the electrode bulk and at the electrode surface written for free charge carriers results in a relationship between the electric potential drop in the electrode phase $\Delta \phi_{\rm M}$ and the surface concentrations of free charge carriers [30]

$$\Delta \phi_{\rm M} = \phi_{\rm P} - \phi_0 = \frac{\psi}{2} \ln \frac{c_{\rm A^+}}{c_{\rm D^-}} \,. \tag{23}$$

We have shown [52] that the concept of electron donors and acceptors allows a simple formulation of electrochemical kinetics in a way analogical to that commonly used in heterogeneous catalysis. Other models for prediction of charge and potential distributions in semiconductors are available in literature, e.g., Refs. [48,49,53].

C. Electrode capacitance

Combining Eqs. (20)–(23), we obtain an explicit expression for the surface concentration of electric charge

$$\sigma = \frac{2c_{\rm tot}F\sqrt{K_{\rm s}}\sinh\left(\frac{\Delta\phi_{\rm M}}{\psi}\right)}{1+2\sqrt{K_{\rm s}}\cosh\left(\frac{\Delta\phi_{\rm M}}{\psi}\right)},\tag{24}$$

and the differential capacitance

$$C_{\rm e} = \frac{2c_{\rm tot}F\sqrt{K_{\rm s}}\left[2\sqrt{K_{\rm s}} + \cosh\left(\frac{\Delta\phi_{\rm M}}{\psi}\right)\right]}{\psi\left[1 + 2\sqrt{K_{\rm s}}\cosh\left(\frac{\Delta\phi_{\rm M}}{\psi}\right)\right]^2}.$$
 (25)

The electrode phase is fully characterized by two parameters c_{tot} and K_s that can be interpreted as the maximal possible concentration of free electric charge carriers on the electrode surface and the ability of these carriers to form electron excess and deficiency regions, respectively. Values of these constants can be in principle evaluated by means of an electrochemical experiment with IPI as will be shown in the next section.

Equations (24) and (25) are odd and even functions, respectively. Hence, the dependencies in Figs. 7 and 8 are



FIG. 7. Dependencies of the surface electric charge (top) and electrode capacitance (bottom) on the potential drop in the electrode. $K_s = 1$.

plotted only for positive potentials. Figure 7 shows that increasing concentration of free charge carriers c_{tot} leads to the increase in the surface concentration of electric charge and the electrode capacitance. For given c_{tot} and K_s values, the charge concentration initially grows with applied potential and flattens out for $\Delta \phi_M > 50$ mV. This behavior reflects



FIG. 8. Dependencies of the surface electric charge (top) and electrode capacitance (bottom) on the potential drop in electrode. $c_{\text{tot}} = 2 \times 10^{-5} \text{mol m}^{-2}$.

the finite number of charge carriers at the electrode surface as expressed by Eq. (22). For that reason, the electrode capacitance reaches its maximum for zero potential. We can see exponential decrease in the electrode capacitance with applied potential for $\Delta \phi_{\rm M} > 50$ mV due to limited pool of electric charge in the electrode phase.

Characteristics of the electrode phase for different K_s values are plotted in Fig. 8. There are relatively insignificant differences between the characteristics for $K_s = 1$ (circles) and $K_s = 1 \times 10^5$ (triangles), which correspond to insensitiveness of the model to K_s when the reaction equilibrium given by Eq. (19) is shifted to the right. The charge carriers then easily appear at the interface even if low potential difference is applied. The surface concentration of electric charge monotonously increases with applied potential and quickly reaches the asymptote given by the limited amount of areas where electric charge can appear [see Eq. (22)]. The capacitance of the electrode phase then monotonously decreases with applied potential.

Qualitatively different behavior is observed when the reaction equilibrium (19) is shifted to the left, i.e., for $K_s = 1 \times 10^{-5}$ (squares in Fig. 8). The surface concentration of electric charge approaches the same asymptote as in the previous cases, however, for $\Delta \phi_M > 200$ mV. This phenomenon can be understood as follows. The concentration of donors and acceptors have to differ significantly according to Eq. (20) to provide high concentration of the electric charge for small K_s . Such a difference appears only when the potential drop $\Delta \phi_M$ is high [see Eq. (23)]. In other words, more energy has to be added to provide the same amount of surface electric charge. This is reflected in the capacitance plot where single local maximum appear for $\Delta \phi_M \approx 150$ mV and also in the process of interface charging as is shown in the next section.

V. CHARGING DYNAMICS

Dynamics of IPI charging can be studied, e.g., by linear sweep voltammetry [51]. When a chosen scan rate is slow, the electrode-electrolyte interface is close to the thermodynamical equilibrium. Especially, when a microelectrode is used as the working electrode, then possible limitation of the charging process by ion transport in the electrolyte phase is avoided [29]. Under such conditions, the electric current response of IPI to a linear voltage sweep can be calculated using equations introduced in Secs. III and IV. To obtain current responses to a high sweep rate, boundary value problem has to be solved, e.g., [52,54,55]. If compared to experimental results, theoretically predicted current-voltage dependencies can be used for the determination of c_{tot} and K_s .

The total difference of electric potential $\Delta \phi_{\rm P} = \phi_{\rm P}$ across the electrode-electrolyte interface is considered in voltammetry experiments. Zero reference potential is set to the electrolyte bulk. The total difference divides into the potential drops in the electrode $\Delta \phi_{\rm M} = \phi_{\rm P} - \phi_0$ and electrolyte $\Delta \phi_0 = \phi_0$, respectively. The response of electric current density to a linear voltage sweep with low scan rate $r \equiv d\phi_{\rm P}/dt$ can be calculated from

$$i = C_{\rm d} \frac{d\phi_0}{dt}$$
 or $i = C_{\rm e} \frac{d\Delta\phi_{\rm M}}{dt}$. (26)

Differential capacitances C_d and C_e depend on ϕ_0 and $\Delta\phi_M$, respectively. However, the distribution of the total potential difference ϕ_P in the electrode and diffuse layer is not *a priori* known. The necessary condition is that the absolute value of the stored electric charge in the electrode phase is equal to that one in the diffuse layer. One can choose any ϕ_P and solve Eqs. (7) and (24) or Eqs. (16) and (24) to get ϕ_0 or $\Delta\phi_M$. The dependence of differential capacitances on the applied voltage is obtained [see Eqs. (9), (18), and (25)]. The current response is finally calculated from Eq. (26). The scan rate r = 0.01 V s⁻¹ was used for the evaluation of all current dependencies showed in Sec. V.

A. Effects of potential drop in electrode phase

When the equilibrium described by Eq. (19) is not shifted too much to the left side and the electrode phase contains vast number of electron mediators, e.g., electrons in thicker layers of metals, then $c_{A^+} \approx c_{D^-}$ even if the surface concentration of electric charge is high. Equation (23) predicts that the potential drop $\Delta \phi_M$ is negligibly small. The potential drop in the diffuse layer ϕ_0 is then approximately equal to the applied potential ϕ_P and the electric current response can be calculated directly from

$$i = C_{\rm d}(\phi_{\rm P})r. \tag{27}$$

The corresponding dependencies of current density calculated for PB and CL models are plotted in Fig. 9 with lines highlighted by squares and circles, respectively.

However, the electrode phase can be made of a semiconductor, doped dielectrics, or thin metal layers where only limited number of electron carriers is available. For example, gold contains about 5.902×10^{28} free electrons per m⁻³ [56], which is equal to the concentration of gold atoms, i.e., one gold atom offers just one electric carrier. The nearest-neighbor distance in the gold lattice is 2.88 Å [50]. The surface concentration of gold atoms and free electric carriers in a gold monolayer



FIG. 9. Dependencies of the current density (left) and relative voltage drop in the electrode phase (right) on the applied voltage. n = -1, $c_{\text{tot}} = 2 \times 10^{-5} \text{ mol m}^{-2}$, $K_{\text{s}} = 1$.

is then $\approx 2 \times 10^{-5}$ mol m⁻². This value was assigned to the parameter c_{tot} .

The electric potential drop in the electrode phase is no longer negligible if the number of free charge carriers is limited. As shown in Fig. 9, PB and CL models demonstrate monotonous increase in the relative potential drop in the electrode phase $f \equiv \Delta \phi_{\rm M}/\phi_{\rm P} \times 100\%$, with the applied voltage $\phi_{\rm P}$. PB model predicts that almost 40% of the total potential drop is localized in the electrode phase if $\phi_{\rm P} = 300$ mV. This fact is not surprising because it is necessary to provide the same amount of electric charge (with the opposite sign) on both sides of the electrode-electrolyte interface. Equation (21) says that efficient separation of electric charge in the electrode phase. The mediator separation emerges only for high $\Delta \phi_{\rm M}$ according to Eq. (23).

The significant increase in $\Delta \phi_{\rm M}$ predicted by PB model is manifested in the linear sweep voltammetry (see Fig. 9). While Eqs. (9) and (27) predict unlimited increase in the differential capacitance and current density, the limited number of charge carriers in the electrode and the decreasing relative potential drop in the diffuse part lead to the appearance of current maximum in the voltammogram (at about 200 mV in Fig. 9) followed by a sharp current decrease. This finding can be understood as behavior of two nonlinear capacitors C_d and $C_{\rm e}$ in series. Qualitative similar behavior was predicted in Ref. [21], who considered the Stern and diffuse layer capacitors in series. The main difference is that Kilic et al. [21] assumed a constant Stern layer capacitance, whereas in our report the electrode capacitance nonlinearly depends on potential drop. Both treatments predict more realistic behavior of the system than the PB model itself because the infinite increase of the capacitance and electric current density is eliminated.

Decrease in the differential capacitance at higher potentials is a spontaneous feature of CL model due to the condensed layer formation (see Fig. 5). It results in a limited accumulation of electric charge at the interface. The increase in the potential drop in the electrode phase is gradual and the relative drop does not exceed 10% under $\phi_P = 300$ mV. Hence, the two voltammograms calculated by CL model for zero and nonzero $\Delta \phi_M$ almost coincide (see Fig. 9).

B. Effect of electrolyte symmetry

Theoretical voltammograms and relative voltage drops for three different electrolytes are plotted in Fig. 10. In general, the peaks predicted by CL model are always smaller (in absolute value) than the peaks given by PB model due to limited ion concentration in the condensed layers. Significant asymmetry of the voltammograms for n = -2 and -3 is given by the noneven dependencies of the differential capacitance on the applied voltage (see Figs. 3 and 5). When the anion valency is higher than the cation valency, higher current peaks are observed in the positive part of voltammogram because anions with higher valency provide more electric charge at the same ion concentration.

High concentration of electric charge in the diffuse or condensed layers formed by multivalent ions forces the separation of electric carriers in the electrode phase, which is accompanied by high potential drop in that phase (see Fig. 10).



FIG. 10. (Color online) Dependencies of the current density (top) and a relative voltage drop in the electrode phase (bottom) on the applied voltage. $c_{\text{tot}} = 2 \times 10^{-5} \text{ mol m}^{-2}$, $K_{\text{s}} = 1$. Predictions given by the CL model, solid lines; PB model, dashed lines.

For the given set of parameters, the relative potential drop in the electrode phase reached $\approx 80\%$ and $\approx 40\%$ according to PB model and CL model predictions, respectively.

C. Effect of electron mediators

The effect of the total concentration of electron mediators in the electrode phase is plotted in Fig. 11. High mediator concentration (squares) leads to $\Delta \phi_M/\phi_P \rightarrow 0$ for ϕ_P ranging from -300 to 300 mV and the voltammogram is simply given by the use of Eqs. (27) and (9) or (18). This suggests that the dynamics of charging process is given only by the processes in the diffuse layer when the electrochemical systems contain IPI with high carrier concentration. This is of course true only for slow scan rates when the diffuse layer is close to the thermal equilibrium.

As described previously, remarkable potential drops in the electrode phase and significant differences between CL an PB model predictions emerge in systems with similar concentration of charge carriers as in the gold atomic monolayer (circles in Fig. 11).

Distinctly different behavior is observed when the carrier concentration is even smaller (triangles). Most of electric potential drop is then localized in the electrode phase. The remaining potential difference is not high enough to induce condensed layer formation. Voltammograms predicted by both models coincide; however, the recorded current density is quite low.

D. Effect of donor-acceptor equilibrium constant

Finally, the effect of K_s on the character of voltammograms and potential drop distribution will be discussed.



FIG. 11. (Color online) Dependencies of the current density (top) and relative voltage drop in the electrode phase (bottom) on the applied voltage. n = -2, $K_s = 1$. Predictions given by the CL model, solid lines; PB model, dashed lines.

Qualitative interpretation of K_s can be expressed as the ability of free electron carriers in a matter to form electron rich or electron poor regions. These regions then accumulate at the interface, affect neighboring environment [57], and possibly enter electrochemical charge transfer (not in IPI).

Higher K_s value at a given c_{tot} results in higher electric current density. The peak current (in absolute value) is higher for $K_s = 1 \times 10^5$ (triangles) than for $K_s = 1$ (circles) (see Fig. 12). The current responses predicted by CL model for these K_s values almost coincide, which reflects insensitiveness of the IPI systems and particularly of the electrode phase to K_s in a broad range as shown in Fig. 8. The potential drop in the electrode phase exhibits single minimum close to zero ϕ_P . With growing $|\phi_P|$, one can see that the potential drop monotonously increases.

However, small K_s value such as 1×10^{-5} (rectangles in Fig. 12) leads to different behavior. For $|\phi_P| < 150$ mV, over 50% of the potential drop is localized in the electrode phase. This is due to high energy that is needed to provide high concentration of electric charge carriers as discussed in Sec. IV C. Hence, for $|\phi_P| < 150$ mV, observed electric current density is low. When energy applied on the interface exceeds a certain value, which is necessary for the formation of charge carriers at the electrode surface, the current density grows. The peak value is reached for $|\phi_P| > 250$ mV, which is higher than 100 mV observed for $K_s = 1 \times 10^5$ or 1. Moreover, the condensed layer in electrolyte is not formed for $K_s = 1 \times 10^{-5}$ and $|\phi_P| < 150$ mV (the PB and CL model predictions coincide) because most of the applied potential emerges in the electrode phase.





FIG. 12. (Color online) Dependencies of the current density (top) and relative voltage drop in the electrode phase (bottom) on the applied voltage. n = -2, $c_{\text{tot}} = 2 \times 10^{-5} \text{ mol m}^{-2}$. Predictions given by the CL model, solid lines; PB model, dashed lines.

VI. CONCLUSIONS

Mathematical models of ideal polarizable electrodeelectrolyte interface have been proposed and tested in this work. Capacitive characteristics of the interface have been derived and used to predict the responses of electric current to linearly varying voltage.

The physical description of the electrolyte phase based on two different models shows that the capacitive behavior of the diffuse layer strongly depends on the polarity of electric field in the case of asymmetric electrolytes. The capacitance minimum is not localized at zero potential. Moreover, the diffuse layer capacitance cannot be considered to be constant even for applied potentials lower than the thermal voltage (≈ 26 mV). As expected, the condensed layer model describes the charging of the diffuse layer more realistically at larger potentials than that based on the Poisson-Boltzmann equation.

The concept of spontaneous formation of the electron donors and acceptors in the electrode phase has been used to derive its capacitive characteristics. If the number of electric charge carriers in the electrode phase is limited, one usually observes decreasing dependence of the differential capacitance on the absolute value of the applied potential. However, when the donor-acceptor equilibrium is shifted more to the basic (uncharged) form of matter, then this dependence exhibits single maximum for certain nonzero value of electric potential. It corresponds to the fact that a large amount of energy is necessary to induce the formation of electric charge carriers.

Finally, current responses to linearly varying voltage applied on the entire electrode-electrolyte interface have been predicted and discussed. Consideration of capacitive properties of both phases allowed to evaluate potential drops in both the electrode and electrolyte. The complex treatment of both sides of the interface confirmed that the charging process in the electrode phase is necessary only when the number of free charge carriers in that phase is limited. The approach reported in this work could be useful for the prediction and understanding of charging processes at special interfaces formed by thin conductive layers that appear, e.g.,

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in supercapacitors, electrochemical sensors, or in photovoltaic applications.

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