

Frumkin–Butler–Volmer Theory and Mass Transfer in Electrochemical Cells¹

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Abstract—An accurate mathematical description of the charge transfer rate at electrodes due to an electrochemical reaction is an indispensable component of any electrochemical model. In the current work we use the generalized Frumkin–Butler–Volmer (gFBV) equation to describe electrochemical reactions, an equation which, contrary to the classical Butler–Volmer approach, includes the effect of the double layer composition on the charge transfer rate. The gFBV theory is transparently coupled to the Poisson–Nernst–Planck ion transport theory to describe mass transfer in an electrochemical cell that consists of two parallel plate electrodes which sandwich a monovalent electrolyte. Based on this theoretical approach we present analytical relations that describe the complete transient response of the cell potential to a current step, from the first initial capacitive charging of the bulk electrolyte and the double layers all the way up to the steady-state of the system. We show that the transient response is characterized by three distinct time scales, namely; the capacitive charging of the bulk electrolyte at the fastest Debye time scale, and the formation of the double layers and the subsequent redistribution of ions in the bulk electrolyte at the longer harmonic and diffusion time scales, respectively.

Keywords: generalized Frumkin–Butler–Volmer equation, electrostatic double layer, Poisson–Nernst–Planck transport theory, transient response, electrochemical cell modeling

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1. INTRODUCTION

Including effects of the double layer composition on the charge transfer rate at electrodes was initiated by Frumkin [1] for one electron proton reduction as an extension to the classical Butler–Volmer equation. Later contributions were e.g. by Parsons [2] who extended Frumkin’s approach to a multiple electron reaction, Itskovich et al. [3] who assumed a constant concentration (and thus a constant chemical potential) for the species in the reduced state, and Franceschetti and MacDonald [4, 5] who mentioned Frumkin’s approach in the context of electrochemical impedance spectroscopy. Calculations for a complete electrochemical cell were first performed by Bonnefont et al. [6] (in [3–5] only single electrode systems were used), and extended in later work by Bazant and coworkers, [7–10] who also introduced the concept of the generalized Frumkin–Butler–Volmer (gFBV) equation [9]. In addition, applications of the Frumkin approach were reported on e.g. corrosion, [11, 12] fuel cells, [13, 14] nano-electrodes, [15] and batteries [16, 17].

To introduce the basic concept of the gFBV theory we first consider the structure of the double layer, which is a combination of the charge free Stern layer and the diffuse layer (DL), as we will explain next. We assume that an ion including its solvation (i.e. hydration) shell cannot approach an electrode infinitesimal close as shown in Fig. 5. As a result, we can identify a plane of closest approach, which coincides with the outer Helmholtz plane. Note that we implicitly neglect ion adsorption on the inner Helmholtz plane, i.e., we assume that no ions break free from their solvation shell. Consequently, we have a charge free layer sandwiched between the electrode and the outer Helmholtz plane, which we refer to as the Stern layer. Next, we assume that an electron can tunnel across the Stern layer, so that we have electron transfer between the ions at the outer Helmholtz plane and the metal of the electrode, and refer to this position as the reaction plane (Fig. 1). Obviously, this view of the reaction plane is very simplistic and in reality many effects can influence its position (and thus the thickness of the Stern layer), such as the surface roughness of the electrode, [18] the presence of an oxide layer, [19] or the distance across which the electrons can tunnel [20]. Therefore we will consider the Stern layer thickness as an adjustable parameter, which we use to study the effect of the double layer composition.

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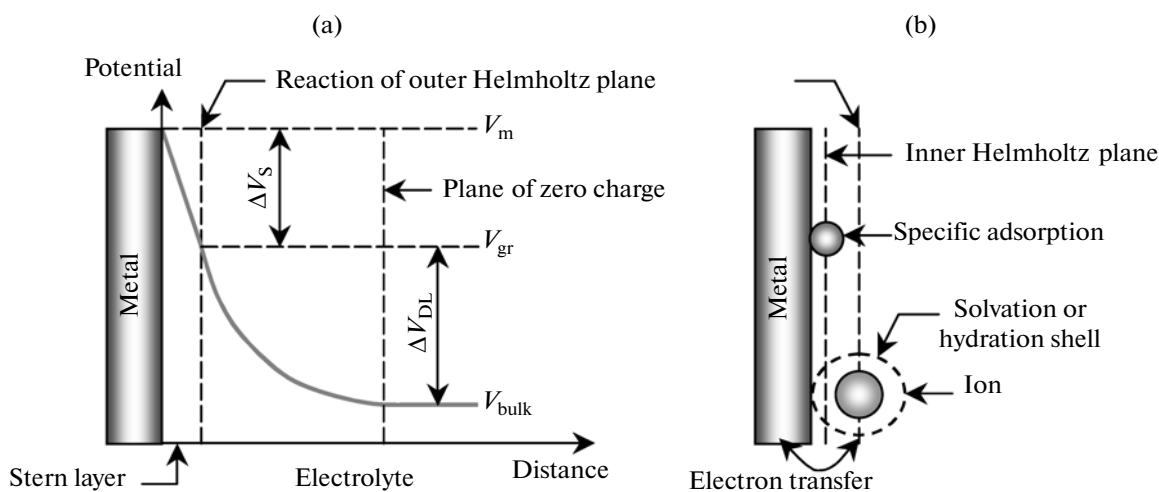


Fig. 1. Schematics of the double layer structure; (a) the potential drop across the double layer, and (b) the plane of closest approach.

Adjacent to the reaction plane a DL containing a non-zero space charge density is formed. As a result we have large electrical field strengths in this layer, while ion concentration gradients counter the forces acting on the ions due to these electrical fields. Including the DLs in an electrochemical model goes beyond the common assumption of electroneutrality, which is ubiquitous in the literature of electrochemical modeling [21–28]. However, including diffuse layers might be important as the electrical potential and ion concentration gradients in these nanoscopic layers are large compared to the more gradual changes in the electroneutral bulk electrolyte. Therefore, the potential drop across the DL might have a significant contribution to the overall cell voltage, while ion concentrations at the reaction plane near the electrode differ from their concentration in the bulk region. Consequently, the formation of DLs can have a large influence on the charge transfer rate at electrodes, a rate which according to the gFBV theory depends on the local potential drop and ion concentration at the reaction plane, as we will explain in the next section.

2. GENERALIZED FRUMKIN–BUTLER–VOLMER EQUATION

Contrary to the classical Butler–Volmer equation [29], where the bulk ion concentration and the potential drop from the metal of the electrode to the bulk electrolyte are the stimuli that drive the reaction, we use the local ion concentration and electrical field strength at the reaction plane in the gFBV equation as these stimuli instead. At the reaction plane we assume an electrochemical reaction of the form, $O + ne^- \rightarrow R$, where we have ideal thermodynamics for the species in the reduced and oxidized states, and use their concen-

tration, c_i , instead of their activities, a_i , to obtain a Faradaic current according to,

$$J_F = K_R c_{O, rp} \exp(-\alpha_R n f \Delta V_S) - K_O c_{R, rp} \exp(\alpha_O n f \Delta V_S), \quad (1)$$

where K_i are rate constants, α_O and α_R are the transfer coefficients ($\alpha_O + \alpha_R = 1$), f is equal to F/RT , with F is Faraday's constant, R is the gas constant and T is temperature, ΔV_S is the potential drop across the Stern layer, subscript rp indicates that the concentration is evaluated at the reaction plane, and subscript O and R denote the oxidized state (or oxidation reaction) and reduced state (or reduction reaction), respectively.

For the potential drop across the Stern layer we require an additional boundary condition, which can be obtained from the electrical field strength at the reaction plane and the properties of the Stern layer as independently proposed by Itskovich et al. [3], Franceschetti and Macdonald [5], and Bonnefont et al. [6]. Namely, the potential drop across the Stern layer follows from the electrical field strength, $E = -\nabla V$, at the reaction plane according to,

$$\Delta V_S = \lambda_S \nabla V|_{rp} \mathbf{n}, \quad (2)$$

where λ_S is the Stern layer thickness, \mathbf{n} is the outward normal vector on the reaction plane, thus pointing out of the electrolyte phase, and subscript rp indicates that the gradient in electrical potential is evaluated at the reaction plane. Substitution of Eq. (2) into Eq. (1) results in the physically intuitive expression [9],

$$J_F = K_R c_{O, rp} \exp(-\alpha_R n \lambda_S f \nabla V \mathbf{n}) - K_O c_{R, rp} \exp(\alpha_O n \lambda_S f \nabla V \mathbf{n}), \quad (3)$$

for the Faradaic charge transfer relation, which only depends on local properties at the reaction plane. Consequently, Eq. (3) clearly shows the difference

between the gFBV equation and the classical Butler–Volmer approach, since for the latter case the potential in the exponential terms is an “over potential” relative to some reference value and condition, while the concentration of species are determined at the bulk-diffuse layer interface. As a result, the classical Butler–Volmer approach cannot be applied to systems where we have charging of the bulk region due to currents above the diffusion limitation [7, 8, 30–32] or the overlap of DLs, such as found in micro- and nanochannels [33–35]. Additionally, the dependence of the electrical potential on the charge transfer rate in the gFBV equation is easier-to-grasp than the “over potential” in the classical Butler–Volmer approach, while it can be transparently incorporated in the boundary conditions of a system without the requirement of a reference or equilibrium condition.

To show the effect of the double layer composition on the charge transfer rate we consider the limit of infinitesimal thin DLs, i.e. the thin-DL limit. The thin-DL limit is a very useful approximation for electrochemical cells with a relatively large electrode spacing compared to the characteristic length scale for the thickness of the DL, i.e. the Debye length,

$\lambda_D = \sqrt{\epsilon_r \epsilon_0 RT/2F^2 c_\infty}$ [7, 8], where ϵ is the permittivity, and c_∞ the ionic strength of the electrolyte. In the thin-DL limit we can use the equilibrium DL properties to describe the ion concentration at the reaction plane [6–8, 30, 36], which result from the Poisson–Boltzmann (PB) ion distribution [36–38],

$$c_{i,gr} = c_{i,bulk} \exp(-z_i f \Delta V_{DL}), \quad (4)$$

where z_i is the valence of ionic species i , ΔV_{DL} is the potential drop across the DL (“zeta potential”), and subscript bulk refers to the bulk region (“plane of zero charge”). Beyond the assumption of ions as point charges and thus the PB distribution, steric effects can play an important role on the structure of the DL at high electrode potentials, so that Eq. (4) changes significantly, as e.g. discussed in [18, 19, 39]. However, these effects are not considered in the current work.

We now substitute the PB ion distribution in Eq. (1) and follow [40], namely; we express the potential drop across the DL as function of the double layer capacitance. We write the double layer capacitance, C_d , as the capacitance of the DL and the Stern layer in series, i.e., $1/C_d = 1/C_{DL} + 1/C_S$, where C_{DL} and C_S refer to the capacitance of the DL and the Stern layer, respectively [19]. The capacitance of two parallel planes is by definition given as $C = \Delta q/\Delta V$, where Δq and ΔV are the difference in charge stored and the electrical potential difference between both planes, respectively. Since the Stern layer remains charge neutral we can write $\Delta V_{DL} = (1 + C_{DL}/C_S)^{-1}(V_m - V_{bulk})$, which relates the potential drop across the DL to the potential drop across the complete double layer, and $\Delta V_S =$

$C_d/C_S(V_m - V_{bulk})$ for the potential drop across the Stern layer. Substitution in Eq. (1) yields

$$J_F = K_R c_{O,bulk} \exp\{-\alpha^* n f (V_m - V_{bulk})\} - K_O c_{R,bulk} \exp\{(1 - \alpha^*) n f (V_m - V_{bulk})\} \quad (5)$$

for the charge transfer rate, where $\alpha^* = \alpha_R \times$

$$\left\{ (C_S/C_{DL} + 1)^{-1} + \frac{z_O}{n\alpha_R} (C_{DL}/C_S + 1)^{-1} \right\}. \text{ Equation (5)}$$

has the same form as the classical Butler–Volmer equation, however, the effective transfer coefficient, α^* , differs from its true value depending on the DL to Stern layer capacitance ratio. The capacitance of the DL and Stern layer per unit area is given as $C_{DL} = -q_{DL}/\Delta V_{DL}$, and $C_S = \epsilon/\lambda_S$, where q_{DL} is the charge stored in the DL. According to the Gouy–Chapman theory the charge stored in the DL equals $q_D = \pm \sqrt{2RT\epsilon} \sum_i c_{i,bulk} \{ \exp(-z_i f \Delta V_{DL}) - 1 \}$ [38], which results in

$$\frac{C_{DL}}{C_S} = \frac{\delta}{f \Delta V_{DL}} \sinh\left(\frac{f \Delta V_{DL}}{2}\right) \quad (6)$$

for the capacitance ratio of a binary electrolyte, i.e. $z_i = \pm 1$, where δ is the Stern layer thickness relative to the Debye length, $\delta = \lambda_S/\lambda_D$. Next, we can identify two limits for the effective transfer coefficient. The first limit is the condition of a zero Stern layer thickness to Debye length ratio, i.e., $\delta \rightarrow 0$, where we have $\alpha^* = z_O/n$. We will refer to this limit as the Gouy–Chapman (GC) limit [7, 9], since in this limit the DL, which is at equilibrium described by the GC theory, dominates the charge transfer rate at the electrode. The second limit is the opposite condition where the Stern layer thickness to Debye length ratio is infinite, i.e., $\delta \rightarrow \infty$, where we thus have $\alpha^* \rightarrow \alpha_R$, and we retain the classical Butler–Volmer equation. We will refer to this limit as the Helmholtz (H) limit [7, 9], since in this limit the potential drop across the double layer exactly equals the potential drop from the metal phase to the reaction, or outer Helmholtz, plane.

Finally, we show results for the effective transfer coefficient as function of the potential drop across the double layer for various values of the Stern layer to Debye length ratios (Fig. 2). To determine the potential drop across the double layer ($\Delta V_{DL} + \Delta V_S = V_m - V_{bulk}$) we use $\Delta V_S = \lambda_D \delta q_{DL}/\epsilon$ [38], where we assume a constant bulk ion concentration, which is valid in the low current regime. Furthermore, we consider an electrochemical reaction involving the transfer of one electron ($\alpha_R = \alpha_O = \frac{1}{2}$, see [7]) with the valence of the ions

in the oxidized state equal to one. The results presented in Fig. 2 show that for $\delta = 0$, i.e. the GC-limit, we have an effective transfer coefficient of 1, while for $\delta = \infty$, (H-limit) we have $\alpha^* = \alpha_R$. For small values of

δ and $V_m - V_{\text{bulk}}$ we find clear deviations from the H-limit, and thus the classical Butler–Volmer equation, while for increasing values of $V_m - V_{\text{bulk}}$ all lines converge towards the H-limit as the capacitance ratio C_{DL}/C_s blows up for high values of the potential drop across the DL (note that $f = \sim 40 \text{ 1/V}$ at $T = 273 \text{ K}$). Consequently, deviations from the classical Butler–Volmer approach are likely to occur at small electrode potentials in combination with small Stern layer thickness to Debye length ratios. However, note that the DL capacitance cannot increase unbounded if steric effects for ion crowding in the DL are taken into account, which result in a maximum capacitance for cell voltages that are not much larger than the zero-voltage [19], and might thus lead to deviations from the H-limit at higher voltages as well.

3. POISSON–NERNST–PLANCK TRANSPORT THEORY

Ion transport in a dilute electrolyte is generally described by the Nernst–Planck (NP) equation, where it is assumed that ions behave as ideal point charges [21]. We can substitute the NP flux equation in a mass balance to obtain,

$$\dot{c}_i = -\nabla \cdot J_i = \nabla \cdot [D_i(\nabla c_i + z_i c_i \nabla V)], \quad (7)$$

where \dot{c}_i is the time-derivative of the ion concentration, J_i is the flux, D_i the diffusion coefficient, z_i the valence of the ions, and V is the local electrostatic potential in volts. In Eq. (7) we do not consider advection of the solvent or chemical reactions within the bulk of the electrolyte. The former is important when e.g. flow cells are considered [14, 35], while the latter cannot be omitted when describing transport of protons and hydroxyl ions due to the self-dissociation of water [13, 41, 42]. The electrical potential in the local-density mean-field approximation is related to the charge density by Poisson's equation

$$\nabla \cdot (\epsilon \nabla V) = -F \sum_i z_i c_i. \quad (8)$$

If we use Eqs. (7) and (8) and combine them with appropriate boundary conditions we obtain a self-consistent set of equations for the description of mass transfer in the bulk electrolyte of an electrochemical cell according to the full Poisson–Nernst–Planck (PNP) transport theory.

The boundary conditions for an applied electrode potential are straightforward and given by

$$V|_{\text{rp}} = V^m - \lambda_s \nabla V \mathbf{n} \quad (9)$$

for the potential at the reaction (outer Helmholtz) plane, while the fluxes of the reacting species are coupled to the charge transfer according to $J_i \mathbf{n} = J_{\text{F}}/F$ and the fluxes of the inert species are zero. The boundary conditions for a system where a constant current is applied are more elaborate and can be derived by con-

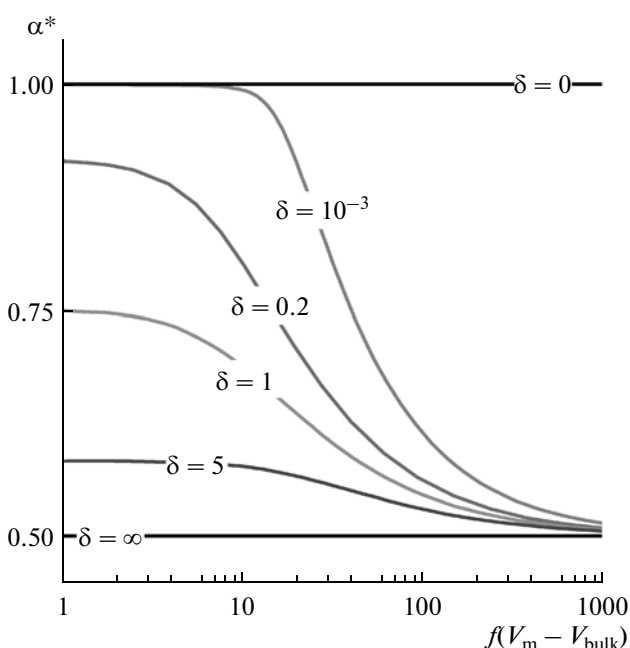


Fig. 2. The effective transfer coefficient for a typical one electron transfer reaction for various values of the Stern layer thickness to Debye length ratios; $z_0 = 1$, $n = 1$, and $\alpha_R = 1/2$.

sidering that in an electrolyte the electrical current is equal to the sum of the ionic conduction current and the Maxwell displacement current, i.e. [6, 11, 43, 44],

$$I = -F \sum_i (z_i J_i) - \epsilon \frac{d}{dt} \nabla V, \quad (10)$$

where the first term represent the conduction current and the second term the Maxwell current. At the electrodes the conduction term equals the Faradaic current, and we obtain [11, 43]

$$\nabla V|_{\text{rp}} = \frac{1}{\epsilon} \int_0^t [J_{\text{F}}(t') \mathbf{n} - I] dt' \quad (11)$$

for the potential gradient at the reaction plane. The contribution of the Faradaic current in Eq. (11) is time-dependent until the steady-state is reached, where it exactly equals the applied current, and the Maxwell current vanish completely.

The assumption of electroneutrality to describe mass transfer is ubiquitous in the literature of electrochemistry [21–28]. Considering Poisson's equation, i.e. Eq. (8), goes beyond this assumption since it couples the electrical potential to the space charge density. Interesting in this equation is the factor between the second derivative of the electrical potential and the space charge density, which is F/ϵ and equals $1.4 \times 10^{14} \text{ V m/mol}$ in aqueous electrolytes. The large magnitude of this term results in an enormous electrical field for even a small excess of space charge, which

will counteract the separation of charges [21]. Also, this term implies that very small deviations from electroneutrality can result in a non-linear electrical potential distribution [21]. Therefore, simply setting the space charge term in Eq. (8) equal to zero and solving the resulting Laplace's equation will result in a flawed model. The proper way of dealing with electroneutrality is to replace Poisson's equation by $\sum_i z_i c_i = 0$. As a result we reduce the number of field variables in our model and make our system of equations more tractable for analytical or numerical solutions. Obviously, electroneutrality is violated near the electrodes where we have the formation of DLs, as here large gradients in electrical potential develop. Consequently, we can only use the electroneutrality assumption in the bulk electrolyte when the DLs are negligibly small compared to feature size of the electrochemical cell, characterized by $\varepsilon = \lambda_D/L \ll 1$, where L is the electrode spacing [6–10, 18, 19, 30, 36, 45–47]. While in addition we need to apply appropriate boundary conditions for the bulk electrolyte, which account for the potential and concentration gradients at interfaces due to the formation of DLs. In general these gradients are well described by the equilibrium properties of the DLs, see [6–10, 18, 19, 30, 36, 45–47].

Note that in many electrochemical cells models the assumption of electroneutrality is accompanied by Laplace's equation for the electrical potential. However, electroneutrality does not imply a Laplacian directly from Poisson's equation, as we will discuss below. Let us consider a system consisting of two parallel electrodes with infinity large area spaced by a finite distance, L , that sandwich a monovalent and binary electrolyte, with the anion and cation concentration denoted as c_a and c_c , respectively. Due to the infinite electrode area we can describe this system using a one-dimensional model with spatial coordinate X , which according to Eq. (7) results in

$$c = \frac{1}{2} \frac{\partial}{\partial X} \left[\left((D_c + D_a) \frac{\partial c}{\partial X} + (D_c - D_a) c f \frac{\partial V}{\partial X} \right) \right] \quad (12)$$

for the mass balance of the dimensionless salt concentration, $c = (c_c + c_a)/2c_\infty$, while for the dimensionless charge density, $\rho = (c_c - c_a)/2c_\infty$, we have

$$\rho = \frac{1}{2} \frac{\partial}{\partial X} \left[\left((D_c - D_a) \frac{\partial c}{\partial X} + (D_c + D_a) c f \frac{\partial V}{\partial X} \right) \right], \quad (13)$$

which approaches zero for $\varepsilon \ll 1$. From Eq. (13) we can obtain an expression for the migration term (i.e. the second term between square brackets), which we substitute in Eq. (12) to obtain [7, 8, 21, 39, 48–52],

$$c = D^* \frac{\partial^2 c}{\partial X^2}, \quad (14)$$

where $D^* = 2D_c D_a / (D_c + D_a)$, which is the ‘‘ambipolar diffusivity’’ of the salt. Eq. (14) now resembles Fick's

second law for the diffusion of neutral species [50, 53], indicating that the salt behaves like one species due to the high forces required to separate the cat- and anions in solution. From Eq. (13) we obtain a replacement for Poisson's equation according to

$$\frac{\partial}{\partial X} \left(c f \frac{\partial V}{\partial X} \right) = - \frac{(D_c - D_a) \partial^2 c}{(D_c + D_a) \partial X^2}, \quad (15)$$

which, by neglecting any redistribution of species and after the Maxwell current died out, follows Ohm's law where the electrical current is given by $I = \kappa \partial_X V$, with the electrolyte conductivity, $\kappa = f F c_\infty (D_c + D_a)$. Though Eq. (15) is derived for our particular system of a binary monovalent electrolyte, similar ‘‘modified Poisson's equations’’ can always be deduced by assuming electroneutrality. In systems where we have a large excess of inert supporting electrolyte the potential is screened across the DLs and a relation for the electrical field in the bulk is not required [46]. Note that in many electrochemical cell models ion redistribution due to mass transfer is neglected, and Eq. (15) condenses to a simple Laplacian equation. However, this is only appropriate under stringent conditions and does not follow from neglecting the space charge density in Eq. (8) directly.

Let us continue our discussion on mass transfer in the system described above by considering the case where we impose a constant electrical current onto the electrodes, while one species is inert and the other electrochemically active at the electrodes. Consequently, we have conservation of the inert species, i.e. $\int c_{\text{inert}} dx = c_\infty L$, so that from Eq. (14) we find that at steady-state we have a linear ion concentration profile of the inert species with a maximum slope equal to $\pm 2c_\infty/L$. When we substitute this concentration profile into the flux equation for the inert species (which equals zero at steady-state) we find that $\pm 2c_\infty/L = -z_i c_i / \partial_X V$, which after substitution into the flux equation for the electrochemically active species leads to the diffusion limiting current, $I_{\text{lim}} = 4FDc_\infty/L$, where D is the diffusion coefficient of the reactive species. Note that we cannot apply a current above this limitation, unless we break the electroneutrality condition and have an expansion of the DLs or introduce another electrode reaction [7, 8, 21, 30, 31, 46].

Next, we consider the diffusion time scale of the system, i.e. $\tau = tL^2/D$. At this time scale the Maxwell current is negligible compared to the conduction current for systems where $\varepsilon_2 \ll 1$ [47]. As a result the applied current to the system equals the conduction current, a situation for which Eq. (14) has an exact solution in terms of an infinite series [50, 51]

$$c(x, \tau) = 1 + 2i_{\text{app}} \left\{ \frac{1}{2} - x - \sum_{n=1}^{n=\infty} \left(f_n \cos \left(\frac{2Nx}{L} \right) \right) \right\}, \quad (16)$$

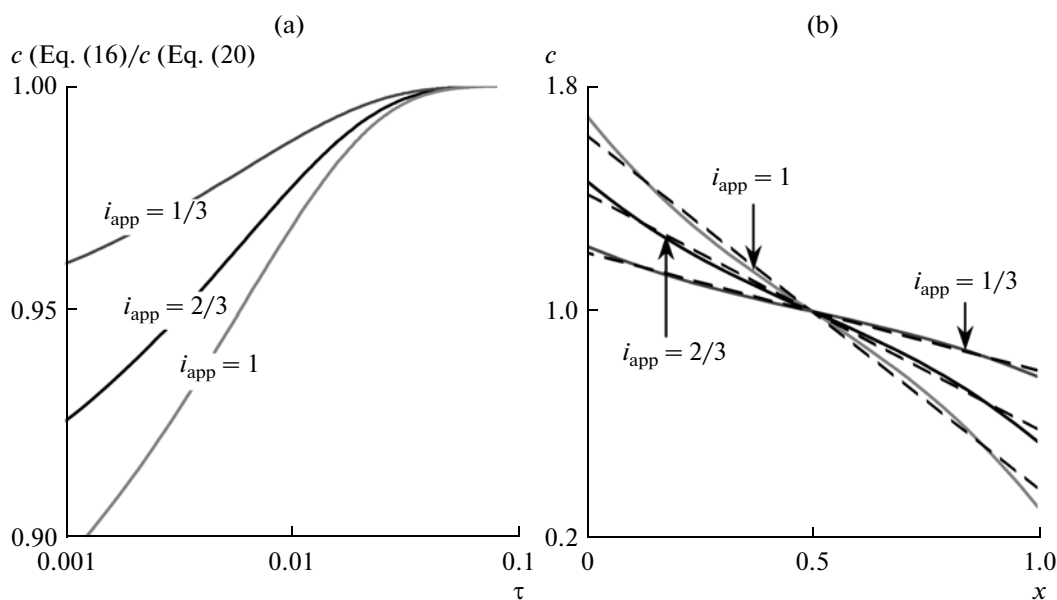


Fig. 3. Comparison between the salt profiles across the cell according to the exact solution and its first order approximation; (a) the relative error between the dimensionless salt concentration at $x = 0$ according to Eq. (16) with $n = 10$ and its first order approximation for $n = 1$, i.e. Eq. (21) as function of dimensionless time τ for i_{app} equal to $1/3$, $2/3$ and 1 ; (b) the concentration profiles corresponding to (a) for $\tau = 0.1$ according to Eq. (16) (full lines) and their linear approximation (dashed lines).

where $f_n = \exp(-4N^2\tau)/N^2$, $N = \frac{1}{2}\pi(2n-1)$, $x = X/L$

and we have scaled the applied current, I_{app} , according to $i_{\text{app}} = I_{\text{app}}/I_{\text{lim}}$. The exponential term in Eq. (16) will vanish for times that are large compared to the diffusion time scale leaving $c(x) = 1 + i_{\text{app}}(1 - 2x)$, which is exactly the classical steady-state solution for planar electrochemical cells [6–9, 26, 45].

Though Eq. (16) will provide an exact solution for the ion redistribution across the cell as function of time for an infinite number of terms, its use for deriving analytical current-voltage relations is limited even for $n = 1$. We will demonstrate this by considering the potential drop across the electroneutral bulk region of the electrolyte. Previously we found that the Maxwell current vanishes at the diffusion time scale [47], so that the conduction current equals the applied electrical current. Converted to the dimensionless parameter introduced above, and writing $\phi = fV$, Eq. (10) becomes $2i_{\text{app}} = c\partial_x\phi$, which results in

$$\Delta\phi_{\text{bulk}} = \phi^0 - \phi^1 = \int_{x=0}^{x=1} \frac{i_{\text{app}}}{c} dx \quad (17)$$

for the potential drop across the bulk region, where superscript 0 and 1 indicate the concentration at $x = 0$ and $x = 1$, respectively. Note that the potential drop across the bulk is positive when positive charge flow from the left to the right through the cell. The integral in Eq. (17) has no exact solution when c is given by

Eq. (16). However, it can be solved rather easily by assuming a linear distribution of species,

$$c(x, \tau) = c^0 + (c^1 - c^0)x, \quad (18)$$

where the concentration at $x = 0$ and $x = 1$ follow from Eq. (16) according to

$$c(\tau) = 1 \pm i_{\text{app}} \left\{ 1 - 2 \sum_{n=1}^{\infty} f_n(\tau) \right\}, \quad (19)$$

where the \pm sign refers to the positive sign at $x = 0$ and the negative sign at $x = 1$, which from $\tau \sim 0.1$ onward can be approximated by the first term of the summation only [47], so that

$$c(\tau) = 1 \pm g(\tau)i_{\text{app}}, \quad (20)$$

where $g(\tau) = 1 - 8/\pi^2 \exp(-\pi^2\tau)$. In Fig. 3a we present results for c according to Eq. (16) relative to Eq. (20). We observe that Eq. (20) is indeed a good approximation for $\tau > 0.1$. In Fig. 3b we show that the corresponding profiles of c are almost linear at $\tau \sim 0.1$. Therefore we will substitute Eq. (20) into Eq. (18) to obtain

$$c(x, \tau) = i_{\text{app}}g(\tau)(1 - 2x) + 1 \quad (21)$$

for the distribution of ions between the two electrodes at times that are comparable to the diffusion time scale. Finally, substituting Eq. (21) into Eq. (17) gives,

$$\Delta\phi_{\text{bulk}} = \frac{2}{g(\tau)} \tanh^{-1}[g(\tau)i_{\text{app}}] \quad (22)$$

for the potential drop across the electroneutral bulk. Combining this potential drop with the potential drops across the DL and the Stern layer will enable us to construct the transient behavior of the cell potential of an electrochemical cell under an imposed current as we will discuss in the next section.

4. DEBYE, HARMONIC, AND DIFFUSION TIME SCALE

In this section we derive analytical relations for the transient response of the cell potential to a step in applied current. These relations include the initial period of capacitive charging of the system as well as the redistribution of ions across the bulk region. As we will show, combining the relations derived here will enable us to construct the complete transient behavior of the cell potential for an electrochemical cell containing a monovalent electrolyte as discussed in the previous section. We consider the case where the cation is the reactive ion, which is formed from the metal of the electrode at $x = 0$ and incorporated again in the metal of the electrode at $x = 1$. Furthermore, we assume that the metal atom concentration is large and not affected by the electrochemical process. Consequently, we can write $K_{O}c_{R} = J_{O}$ for the oxidation rate.

First, we derive an expression for the capacitive charging of the bulk region of the electrochemical cell. In the absence of ion redistribution, i.e. $c(x, \tau) = 1$ and $\rho(x, \tau) = 0$, the potential drop across the bulk region is linear and equals $\Delta\varphi_{\text{bulk}} = -\partial_x\varphi$, so that from Eq. (10) converted to dimensionless parameters we obtain the differential equation, $d\tau = \varepsilon^2/(2I_{\text{app}} + \Delta\varphi_{\text{bulk}})d\Delta\varphi_{\text{bulk}}$, which results in

$$\Delta\varphi_{\text{bulk}} = 2i_{\text{app}}[1 - \exp(-\tau/\varepsilon^2)] \quad (23)$$

for the initial charging of the bulk region. Note that τ/ε^2 in Eq. (23) represents the Debye time scale, which is a material property of the electrolyte and has a characteristic value for aqueous solutions in the range of ns to μs [36].

Next, we derive an expression for the potential drop across the double layers. To do this we consider the current at the reaction plane, i.e., Eq. (11), from which we obtain,

$$\frac{d\Delta\varphi_S}{d\tau} = \pm \frac{2\delta(j_F - i_{\text{app}})}{\varepsilon} \quad (24)$$

for the time derivative of the potential drop across the Stern layer, where the \pm -sign refers to the positive value at position $x = 1$ and the negative value at position $x = 0$, and $j_F = J_F/I_{\text{lim}}$, which is the Faradaic current scaled to the diffusion limiting current. We assume that the DLs are in quasi-equilibrium (valid for $\varepsilon \ll 1$) and are thus described by the PB distribution according to Eq. (4), while again no redistribution of

ions in the bulk region occurs, so that the Faradaic current equals,

$$\pm j_F = k_R \exp\left(-\frac{1}{2}\Delta\varphi_S - \Delta\varphi_{\text{DL}}\right) - j_O \exp\left(\frac{1}{2}\Delta\varphi_S\right), \quad (25)$$

where $\Delta\varphi_{\text{DL}} = 2\sinh^{-1}\left(\frac{\Delta\varphi_S}{2\delta}\right)$ [38], and the reaction

rate constants are scaled to the diffusion limiting current, $k_R = K_R c_{\infty}/I_{\text{lim}}$ and $j_O = J_O/I_{\text{lim}}$. Note that in Eq. (24) the dynamics is characterized by the time scale τ/ε , which is the harmonic time scale of the system [36]. Consequently, we have the charging of the bulk region at the Debye time scale, while the charging of the DLs is at the longer harmonic time scale, followed by the redistribution of ions at the longest diffusion time scale.

Finally, we can solve Eqs. (24) and (25) numerically and combine the results for $\Delta\varphi_S$ and $\Delta\varphi_{\text{DL}}$ with the result for $\Delta\varphi_{\text{bulk}}$ of Eq. (23) according to

$$\begin{aligned} \varphi_{\text{cell}} &= [\Delta\varphi_S + \Delta\varphi_{\text{DL}}]_{x=0} + \Delta\varphi_{\text{bulk}} \\ &= [\Delta\varphi_S + \Delta\varphi_{\text{DL}}]_{x=1} \end{aligned} \quad (26)$$

to obtain the initial cell potential as function of time. Next we discuss a simplified solution of Eq. (24) in the limit of small potential drops across the double layer. For small potential drops across the Stern layer, which e.g. occur in case of fast electrode kinetics, we can linearize the Faradaic current, such that

$$\pm j_F = -\frac{\Delta\varphi_S}{2} \left[k_R \left(\frac{\delta + 2}{\delta} \right) + j_O \right] + i^*, \quad (27)$$

where $i^* = k_R - j_O$, which after substitution into Eq. (24) and integration results in,

$$\begin{aligned} \Delta\varphi_S &= \pm \frac{2\delta(i_{\text{app}} - i^*)}{k_R(\delta + 2) + j_O\delta} \\ &\times \left\{ \exp\left(-(k_R(\delta + 2) + j_O\delta) \frac{\tau}{\varepsilon} \right) - 1 \right\} \end{aligned} \quad (28)$$

for the potential drop across the Stern layer, where the \pm -sign again refers to the positive value at position $x = 1$ and the negative value at position $x = 0$. For small values of $\Delta\varphi_S$ we can derive the potential drop across the DL from Eq. (28) according to $\Delta\varphi_{\text{DL}} = \Delta\varphi_S/\delta$, which after substitution of Eqs. (23) and (28) in Eq. (26) results in an analytical description of the initial capacitive charging of the system for low potential drops across the double layer. However, note that for a large unbalance in the gFBV equation, i.e., when $|k_R - j_O| \gg 0$, the assumption of a small potential drop across the double layer is not satisfied, even for fast electrode kinetics, due to the relatively high open cell potential. Next, we assume that $k_R = j_O = k$ at both

reaction planes, so that an unbalance in the gFBV equation is absent. As result we obtain from Eqs. (23), (26) and (28),

$$\varphi_{\text{cell}} = 2i_{\text{app}} \times \left\{ \left[1 - \exp(-\tau/\varepsilon^2) \right] - \frac{1}{k} \left[\exp\left(-2k(\delta+1)\frac{\tau}{\varepsilon}\right) - 1 \right] \right\} \quad (29)$$

for the cell potential as function of time up to the harmonic time scale.

Solutions for the cell potential at the diffusion time scale were already presented in [47] for both the GC- and H-limit as previously discussed in the current work. Here we restate the results presented in [47] and briefly describe their derivation. First we consider the gFBV equation for the electrochemical charge transfer, which equals the applied current at the diffusion time scale, and where we again use the PB relation, i.e. Eq. (4), to obtain,

$$\pm j_{\text{F}} = \pm i_{\text{app}} = k_{\text{R}} c_{\text{m}} \exp\left(-\frac{1}{2}\Delta\varphi_{\text{S}} - \Delta\varphi_{\text{DL}}\right) - j_{\text{O}} \exp\left(\frac{1}{2}\Delta\varphi_{\text{S}}\right), \quad (30)$$

where c_{m} is the concentration at the very edge of the bulk region and subscript m either denotes the anode side (A) at $x=0$ or the cathode side (C) at $x=1$. Equation (30) differs from Eq. (25) in not assuming that the ion concentration in the bulk remains constants but can vary in time. Note that in many models a charge transfer relation is used with some fixed pre-term for the reaction rate constant that does not account for ion redistribution due to mass transfer. Consequently, the applicability of these models is limited to the relatively small field where ion redistribution is negligible. Returning to our limiting cases, we can derive the potential drop across the double layer from Eq. (30) as function of the applied potential and ion concentration at the very edge of the bulk region. In the GC-limit the Stern layer does not sustain any voltage drop, so that from Eq. (30) we obtain,

$$\Delta\varphi_{\text{DL, GC}} = \ln\left(\frac{k_{\text{R, m}} c_{\text{m}}}{j_{\text{O, m}} \mp i_{\text{app}}}\right), \quad (31)$$

while for the H-limit, where the potential across the DL equals zero, we obtain,

$$\Delta\varphi_{\text{S, H}} = 2 \ln\left(\frac{\pm i_{\text{app}} + \sqrt{i_{\text{app}}^2 + 4j_{\text{O, m}} k_{\text{R, m}} c_{\text{m}}}}{2j_{\text{O, m}}}\right). \quad (32)$$

Finally, we can combine Eqs. (20), (22), and (26) with either Eqs. (31) or (32) to obtain

$$\varphi_{\text{cell, GC}} = \varphi_0 + \ln\left(\frac{1 + i_{\text{app}}/j_{\text{O, C}}}{1 - i_{\text{app}}/j_{\text{O, A}}}\right) + 2\frac{1+g}{g} \tanh^{-1}[gi_{\text{app}}] \quad (33)$$

for the cell potential in case of the GC-limit and,

$$\varphi_{\text{cell, H}} = \varphi_0 + 2 \sinh^{-1}\left(\frac{i_{\text{app}}}{\sqrt{\beta_{\text{A}}(1 + gi_{\text{app}})}}\right) + 2 \sinh^{-1}\left(\frac{i_{\text{app}}}{\sqrt{\beta_{\text{C}}(1 - gi_{\text{app}})}}\right) + 2\frac{1+g}{g} \tanh^{-1}[gi_{\text{app}}] \quad (34)$$

for the H-limit, where $\beta_{\text{m}} = 4j_{\text{O, m}} k_{\text{R, m}}$ and $\varphi_0 = \ln(j_{\text{O, C}} k_{\text{R, A}} / j_{\text{O, A}} k_{\text{R, C}})$, which is the open cell potential. Equations (33) and (34) become accurate after $\tau \sim 0.1$ when the ion concentration and the potential drop across the bulk region are well predicted by Eqs. (20) and (22), respectively. For long times, i.e. $\tau \rightarrow \infty$, we obtain the steady-state solutions reported in [9] except for a sign reversal of all terms due to the reversed definition of the cell potential in [9]. It is interesting to see that the difference between Eqs. (33) and (34) vanishes when the kinetic rate constants become very high. Namely, the second term in Eq. (32) becomes negligible when $j_{\text{O, m}} \gg i$, and the same holds for the second and third term of Eq. (34) for $\beta_{\text{m}} \gg i^2/(1 \pm g(\tau)i)$. In addition, it was observed that the solutions for increasing thickness of the Stern layer converges rapidly to the H-limit [47]. Therefore, for higher values of the Stern layer thickness the difference between the classical BV and the gFBV equation is indistinguishable. An effect which is similar to that presented in Fig. 2.

Results that show the correspondence between the full PNP-gFBV theory and the simplified models derived above are presented in Fig. 4a. The full PNP-gFBV model results are computed by implementing the dimensionless equivalents of Eqs. (7) and (8) with boundary conditions according to Eq. (11) in the commercial finite element code COMSOL (a more detailed description of this procedure can be found in [47]). The results show that even at a relatively low value of the kinetic constant, namely; $k=0.3$, the simplified model according to Eq. (29) is a good approximation for the transient current, while for $k=0.1$ the solution based on solving the simple differential equation of Eq. (24) gives a good approximation. In addition we can use the relations for the cell potential at the diffusion time scale, i.e. Eqs. (33) and (34), in combination with either Eq. (24) or (29) to construct the whole start-up behavior from $\tau=0$ up to the steady-state of the electrochemical cell (Fig. 4b). Here we clearly see that for the model parameters considered here ($i_{\text{app}}=0.75$, $k=2$, and $\delta=10$) the GC- and

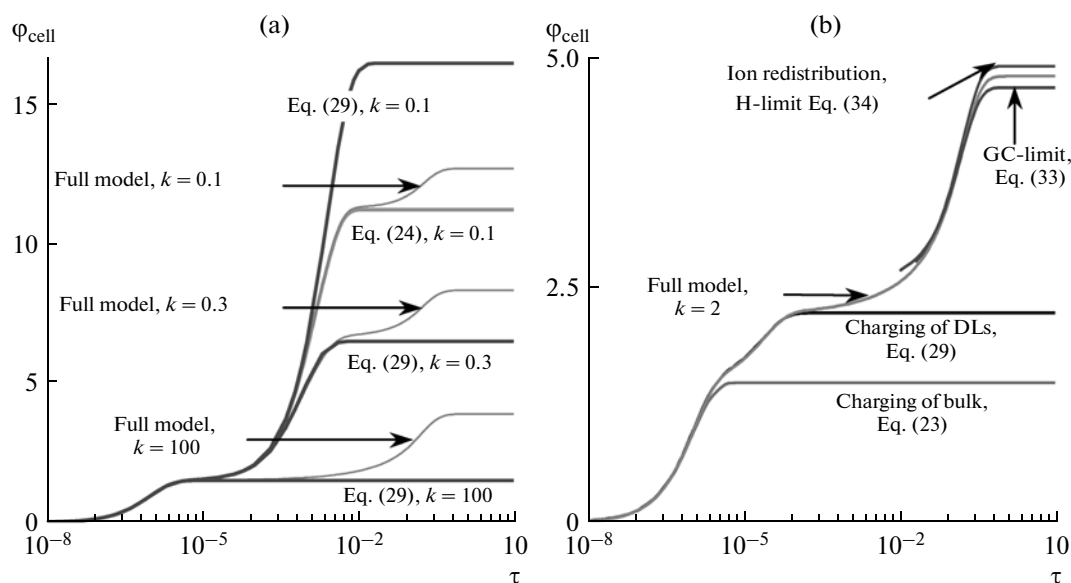


Fig. 4. Cell potential as function of dimensionless time; (a) comparison between the simplified models, i.e., Eqs. (24) and (29), and the full model for $i = 0.75$, $\varepsilon = 10^{-3}$, $k = 0.1-100$ and $\delta = 1$; (b) the complete transient behavior from the composition of the simplified models for (i) charging the bulk region, Eq. (23), (ii) charging the DLs, Eq. (24), and (iii) the ion redistribution across the bulk region for the GC- and H-limit, i.e. (32) and (33), respectively, for $i = 0.75$, $\varepsilon = 10^{-3}$, $k = 2$ and $\delta = 10$.

H-limit give a lower and upper boundary for the time-dependent cell potential that are sufficiently close together to fairly accurately predict the response for an arbitrary value of the Stern layer thickness δ .

To summarize, we first have the capacitive charging of the bulk region at the Debye time scale, followed by the formation of the DLs at the harmonic time scale, while finally the cell potential further evolves due to the redistribution of ions at the diffusion time scale. Consequently, the transient behavior of the cell potential of an electrochemical cell in response to an applied electrical current proceeds at three distinct time scales.

CONCLUSIONS

We have used the generalized Frumkin–Butler–Volmer (gFBV) equation to describe the charge transfer rate due to an electrochemical reaction at an electrode. In the gFBV equation it is assumed that the electrochemical reaction proceeds at a predefined plane near the electrode. We have shown that for an infinitely large spacing between this reaction plane and the metal of the electrode relative to the Debye length, which is a characteristic length scale for the diffuse layer containing a non-zero space charge density, we obtain the classical Butler–Volmer equation as the correct limit of the gFBV equation. In the opposite limit, where the reaction plane coincides with the metal electrode, the charge transfer rate is dominated by the properties of the diffuse layer. Consequently, in this case the gFBV deviates significantly from the classical Butler–Volmer equation, since the latter equa-

tion does not consider the non-zero space charge density in the diffuse layer.

In addition we have shown that the gFBV equation more naturally combines with the Poisson–Nernst–Planck (PNP) transport theory for ionic species than the classical Butler–Volmer equation. From the full PNP–gFBV model we have derived analytical relations for the transient behavior of the cell potential of an electrochemical in response to a step in the applied current. It followed from these relations that the evolution of the cell potential proceeds at three distinct time scales. Namely; (i) the Debye time scale for the capacitive charging of the electroneutral bulk region, (ii) the harmonic time scale for the formation of the diffuse layer, and (iii) the diffusion time scale for the redistribution of ions across the cell. We showed that by combining the solutions for all three time scales we can construct the complete transient behavior of the cell, from the very initial capacitive charging all the way up to the steady state.

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REFERENCES

1. Frumkin, A., *Z. Physik. Chem., Ser. A*, 1933, vol. 164, p. 121.
2. Parsons, R., *Adv. Electrochem. Electrochem. Eng.*, 1961, vol. 1, p. 1.

3. Itskovich, E.M., Kornyshev, A.A., and Vorotyntsev, M.A., *Physica Status Solidi, Ser. A*, 1977, vol. 39, p. 229.
4. Franceschetti, D.R. and Macdonald, J.R., *J. Electroanal. Chem.*, 1978, vol. 87, p. 419.
5. Franceschetti, D.R. and Macdonald, J.R., *Proc Third Symposium on Electrode Processes*, Boston, USA, 1979, p. 94.
6. Bonnefont, A., Argoul, F., and Bazant, M.Z., *J. Electroanal. Chem.*, 2001, vol. 500, p. 52.
7. Bazant, M.Z., Chu, K.T., and Bayly, B.J., *SIAM J. Appl. Math.*, 2005, vol. 65, p. 1463.
8. Chu, K.T. and Bazant, M.Z., *SIAM J. Appl. Math.*, 2005, vol. 65, p. 1485.
9. Biesheuvel, P.M., van Soestbergen, M., and Bazant, M.Z., *Electrochimica Acta*, 2009, vol. 54, p. 4857.
10. Biesheuvel, P.M., Franco, A.A., and Bazant, M.Z., *J. Electrochem. Soc.*, 2009, vol. 156, p. B225.
11. Murphy, W.D., Manzanares, J.A., Mafé, S., and Reiss, H., *J. Phys. Chem.*, 1992, vol. 96, p. 9983.
12. van Soestbergen, M., Mavinkurve, A., Rongen, R.T.H., Jansen, K.M.B., Ernst, L.J., and Zhang, G.Q., *Electrochimica Acta*, 2010, vol. 55, p. 5459.
13. Franco, A.A., Schott, P., Jallut, C., and Maschke, B., *Fuel Cells*, 2007, vol. 7, p. 99.
14. Sprague, I.B. and Dutta, P., *Numerical Heat Transfer, Ser. A*, 2011, vol. 59, p. 1.
15. He, R., Chen, S., Yang, F., and Wu, B., *J. Phys. Chem., Ser. B*, 2006, vol. 110, p. 3262.
16. Becker–Steinberger, K., Funken, S., Landstorfer, M., and Urban, K., *ECS Trans.*, 2010, vol. 25, p. 285.
17. Bower, A.F., Guduru, P.R., and Sethuraman, V.A., *J. Mech. Phys. Solids*, 2011, vol. 59, p. 804.
18. Bazant, M.Z., Kilic, M.S., Storey, B.D., and Ajdari, A., *Adv. Coll. Int. Sci.*, 2009, vol. 152, p. 48.
19. Kilic, M.S., Bazant, M.Z., and Ajdari, A., *Phys. Rev., Ser. E*, 2007, vol. 75, p. 021502.
20. Gavaghan D.J. and Feldberg S.W., *J. Electroanal. Chem.*, 2000, vol. 491, p. 103.
21. Newman, J.S., *Electrochemical Systems*, Prentice-Hall, Englewood Cliffs, 1973.
22. Bard, A.J. and Faulkner, L.R., *Electrochemical Methods*, New York: Wiley, 2001.
23. Cui, F., Presuel-Moreno, F.J., and Kelly, R.G., *Corrosion Sci.*, 2005, vol. 47, p. 2987.
24. Presuel-Moreno, F.J., Wang, H., Jakab, M.A., Kelly, R.G., and Scully, J.R., *J. Electrochem. Soc.*, 2006, vol. 153, p. B486.
25. Danilov, D. and Notten, P.H.L., *Electrochimica Acta*, 2008, vol. 53, p. 5569.
26. Danilov, D. and Notten, P.H.L., *J. Power Sources*, 2009, vol. 189, p. 303.
27. Zelinsky, A.G. and Pirogov, B.Ya., *Electrochimica Acta*, 2009, vol. 54, p. 6707.
28. Van Damme, S., Maciel, P., van Parys, H., Deconinck, J., Hubin, A., and Deconinck, H., *Electrochem. Commun.*, 2010, vol. 12, p. 664.
29. Vetter, K.J., *Electrochemical Kinetics*, N.Y.: Academic Press, 1967, p. 117.
30. Smyrl, W.H. and Newman, J., *Trans. Faraday Soc.*, 1967, vol. 63, p. 207.
31. Rubinstein, I. and Shtilman, L., *Chem. Soc., Faraday Trans., 2*, 1979, vol. 75, p. 231.
32. Yariv, E., *Phys. Rev., Ser. E*, 2009, vol. 80, p. 051201.
33. Mala, Gh.M., Li, D., Werner, C., Jacobasch, H.-J., and Ning, Y.B., *Int. J. Heat Fluid Flow*, 1997, vol. 18, p. 489.
34. Stein, D., Kruithof, M., and Dekker, C., *Phys. Rev. Lett.*, 2004, vol. 93, p. 035901.
35. Biesheuvel, P.M., Fu, Y., and Bazant, M.Z., *Russ. J. Electrochem.*, 2012, vol. 48, no. 6.
36. Bazant, M.Z., Thornton, K., and Ajdari, A., *Phys. Rev., Ser. E*, 2004, vol. 70, p. 021506.
37. Biesheuvel, P.M., *J. Colloid Interface Sci.*, 2001, vol. 238, p. 362.
38. Mohilner, D.M., *Electroanalytical Chemistry*, Vol. 1, Bard, A.J., Ed., N.Y.: Dekker, 1966, p. 241.
39. Biesheuvel, P.M. and van Soestbergen, M., *J. Coll. Int. Sci.*, 2007, vol. 316, p. 490.
40. Vetter, K.J., *Electrochemical Kinetics*, New York: Academic Press, 1967.
41. Turjanski, P., Olaiz, N., Abou-Adal, P., Suárez, C., Risk, M., and Marshall, G., *Electrochimica Acta*, 2009, vol. 54, p. 6199.
42. Jacobs, R.A., Sengun, M.Z., Hicks, R.E., and Probststein, R.F., *J. Environ. Sci. Health.*, 1994, vol. 29, p. 1933.
43. Manzanares, J.A., Murphy, W.D., Mafé, S., and Reiss, H., *J. Phys. Chem., Ser. B*, 1993, vol. 97, p. 8524.
44. Moya, A.A., Castilla, J., and Homo, J., *J. Phys. Chem.*, 1995, vol. 99, p. 1292.
45. Prieve, D.C., *Colloids Surf., Ser. A*, 2004, vol. 250, p. 67.
46. van Soestbergen, M., *Electrochimica Acta*, 2010, vol. 55, p. 1848.
47. van Soestbergen, M., Biesheuvel, P.M., and Bazant, M.Z., *Phys. Rev., Ser. E*, 2010, vol. 81, p. 021503.
48. Levich, V.G., *Physicochemical Hydrodynamics*, Printice-Hall, 1962, p. 281.
49. Rosenbrugh, T.R. and Lash Miller, W., *J. Phys. Chem.*, 1910, vol. 14, p. 816.
50. Crank, J., *The Mathematics of Diffusion*, Clarendon, 1990, p. 61.
51. Carslaw, H.S. and Jaeger, J.C., *Conduction of Heat in Solids*, Oxford University Press, 2003, p. 113.
52. Tobias, C.W., Eisenberg, M., and Wilke, C.R., *J. Electrochem. Soc.*, 1952, vol. 99, p. 359C.
53. Deen, W.M., *Analysis of Transport Phenomena*, Oxford, 1998.