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On the Deviation of Electro-Neutrality in Li-Ion Battery Electrolytes

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The electro-neutrality assumption for Li-ion battery electrolytes has been mathematically investigated. A general system of equations describing the development of ionic concentration gradients in simple binary electrolytes is derived. Considering that the overpotentials and the concentration gradients across the electrolyte are most dominant under steady-state (dis)charging, the analyses have been performed under these limiting conditions. It was found that deviations from electro-neutrality in terms of ionic concentrations are extremely small and do not exceed 10⁻⁷% under normal (dis)charging conditions. Nevertheless this small deviation is responsible for development of an electric field with considerable magnitude. Therefore, a rearrangement of standard Nernst-Planck equations is essential to accurately model these processes at different scales.

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Highly efficient Li-ion batteries are nowadays widely applied in home appliances, wireless communications, residential storage and advanced hybrid and full electrical vehicles. The ionic conductivity of the electrolyte plays an important role in the functioning of these batteries.¹⁻³ Therefore an appropriate mathematical description of the electrolyte forms an essential part in all Li-ion battery models.⁴⁻⁷ The electro-neutrality assumption is commonly accepted to describe the ionic transportation properties in these Li-based systems.⁸ This has, however, been criticized because of the apparent disagreement between the assumed zero net charge in the electrolyte and the non-uniform electric field, resulting from that approximation.

There are a number of papers dealing with deviations from electro-neutrality. The separation of charge at the interface between a growing metallic crystal and a solution has been studied in.⁹ Because of the mobility difference between electrons in the solid and ions in the solution, an electrical double layer, breaching the local electro-neutrality conditions, is formed at the interface. This electrical double layer has a thickness comparable to that of the Debye length. The Nernst-Planck approach has been corrected by taking into account the conservation law of mass for the electrolyte and the balance equations for ionic momentum. No violation of electro-neutral conditions was found in the bulk of the electrolyte. However, electrical double layer thicknesses of only about 10 nm at the electrode/electrolyte interface were found.¹⁰ An excess of positive charge was reported by Zabolotskii, et al. when studying the ionic transportation through a three-layered membrane.¹¹ The effects of the diffuse double layer charge on the electrochemical charge transfer rates in galvanic cells have been investigated by Biesheuvel, et al.¹² Without assuming local electro-neutrality the authors combined a generalized Frumkin-Butler-Volmer boundary condition to describe the reaction kinetics with the Poisson-Nernst-Planck flux equations. Numerical solutions were compared to analytical results in the thin electrical double layers. Concentration and potential profiles as function of the Stern and Debye lengths were studied and two kind of the limiting cases, i.e. Gouy-Chapman and Helmholtz, were considered and the thicknesses were found to be of the order of several Stern and Debye lengths, respectively. A comprehensive review can be found in.¹³ The influence of the electro-neutrality approximation on steady-state voltammetry has been investigated in.^{14,15} The steady-state analysis for the lead-acid batteries was performed in.^{16,17} Steady-state concentration gradients in Li-ion batteries has also been experimentally studied.^{18,19}

In the present paper the concentration gradients and electric fields for simple binary electrolytes in Li-ion batteries are mathematically investigated under steady-state, constant current, (dis)charging conditions. In a typical Li-ion battery, the distance between the electrodes is of the order of magnitude of hundreds of thousands Debye lengths. As the focus of the present work is concentrated on the bulk of the electrolyte, the interfacial effects at electrode/electrolyte interfaces are therefore omitted. A simple and universal method to find the deviations from electro-neutrality by successive iterations is proposed. The influence of the (dis)charging current and the electrolyte salt concentration has been investigated.

Theoretical Considerations

Model set-up.— Fig. 1 illustrates general layout of a conventional Li-ion battery. LiCoO₂ serves as positive electrode material, while lithiated graphite is used for the negative electrode. For the positive electrode the following electrochemical description holds

Eq. 1 implies that Li-ions are extracted from the positive electrode during charging and inserted back during discharging. In contrast, Li ions are inserted into graphite during the charging and extracted during discharging, which is described by

the electrochemical charge transfer reactions (Eqs. 1 and 2), therefore, require Li-ions to cross the electrolyte under current flowing conditions (see Fig. 1). The electrolyte in Li-ion batteries is based on a Li-containing salt, e.g. LiPF₆ or LiClO₄.

Denote the concentration of the Li⁺ ions in the electrolyte by $c_{\text{Li}^+}(y, t)$ and the concentration of PF₆⁻ by $c_{\text{PF}_6^-}(y, t)$. In absence of convection the following Nernst-Planck definition²⁰ of fluxes for Li⁺ and PF₆⁻ ions holds

$$J_j(y, t) = -D_j \frac{\partial c_j}{\partial y} + \frac{z_j F}{RT} D_j c_j E, \quad [3]$$

where $J_j(y, t)$ is the flux of species j [mol · m⁻² · s⁻¹] at position y at any moment of time t , $\frac{\partial c_j}{\partial y}$ the concentration gradient [mol · m⁻⁴], D_j is the diffusion coefficient of j [m² · s⁻¹], $E(y, t)$ is the electric field

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Figure 1. Schematic representation of a conventional Li-ion battery, indicating the movements of Li-ions in the LiPF₆ salt-containing electrolyte during charge and discharge.

[V · m⁻¹] and z_j is the valence state of each species. F is Faraday's constant (96485 C · mol⁻¹), R the gas constant (8.3145 J · mol⁻¹ · K⁻¹) and T is the temperature of the electrolyte [K].

The following coupled partial differential equations (PDEs) describe evolution of concentrations of Li⁺ and PF₆⁻ ions inside the electrolyte layer

$$\frac{\partial c_{Li^+}}{\partial t} = -\frac{\partial J_{Li^+}}{\partial y}, \quad [4.1]$$

$$c_{Li^+}(y, 0) = c_0, \quad [4.2]$$

$$J_{Li^+}(0, t) = -\frac{I_{LiC_6}(t)}{z_{Li^+}FA}, \quad [4.3]$$

$$J_{Li^+}(L, t) = \frac{I_{LiCoO_2}(t)}{z_{Li^+}FA}, \quad [4.4]$$

and

$$\frac{\partial c_{PF_6^-}}{\partial t} = -\frac{\partial J_{PF_6^-}}{\partial y}, \quad [5.1]$$

$$c_{PF_6^-}(y, 0) = c_0, \quad [5.2]$$

$$J_{PF_6^-}(0, t) = 0, \quad [5.3]$$

$$J_{PF_6^-}(L, t) = 0. \quad [5.4]$$

Eqs. 4.1 and 5.1 constitute mass conservation law. Initial-value conditions Eqs. 4.2 and 5.2 show that at $t = 0$ all concentration profiles are flat, constant and equal to c_0 . $I_{LiC_6}(t)$ and $I_{LiCoO_2}(t)$ are the currents transferred across the surfaces of the negative and positive electrodes, accordingly, and A is the surface area [m²]. Eqs. 4.3, 4.4 and Eqs. 5.3, 5.4 represent the flux conditions of Li⁺ and PF₆⁻ ions, respectively, at both electrode/electrolyte interfaces. Considering the charging process, the reduction current at the negative electrode is defined as negative while the oxidation current at the positive electrode is defined positive. Obviously, for discharging the current definitions are reversed.

Introducing the first derivative of Eq. 3 into Eqs. 4 and 5 and taking into account that $z_{Li^+} = -z_{PF_6^-} = 1$ leads to

$$\frac{\partial c_{Li^+}}{\partial t} = D_{Li^+} \frac{\partial^2 c_{Li^+}}{\partial y^2} - D_{Li^+} \frac{F}{RT} \frac{\partial (c_{Li^+} E)}{\partial y}, \quad [6.1]$$

$$c_{Li^+}(y, 0) = c_0, \quad [6.2]$$

$$D_{Li^+} \frac{\partial c_{Li^+}(0, t)}{\partial y} - D_{Li^+} \frac{F}{RT} c_{Li^+}(0, t) E(0, t) = -\frac{I_{LiC_6}(t)}{FA}, \quad [6.3]$$

$$D_{Li^+} \frac{\partial c_{Li^+}(L, t)}{\partial y} - D_{Li^+} \frac{F}{RT} c_{Li^+}(L, t) E(L, t) = \frac{I_{LiCoO_2}(t)}{FA}, \quad [6.4]$$

and

$$\frac{\partial c_{PF_6^-}}{\partial t} = D_{PF_6^-} \frac{\partial^2 c_{PF_6^-}}{\partial y^2} + D_{PF_6^-} \frac{F}{RT} \frac{\partial (c_{PF_6^-} E)}{\partial y}, \quad [7.1]$$

$$c_{PF_6^-}(y, 0) = c_0, \quad [7.2]$$

$$D_{PF_6^-} \frac{\partial c_{PF_6^-}(0, t)}{\partial y} + D_{PF_6^-} \frac{F}{RT} c_{PF_6^-}(0, t) E(0, t) = 0, \quad [7.3]$$

$$D_{PF_6^-} \frac{\partial c_{PF_6^-}(L, t)}{\partial y} + D_{PF_6^-} \frac{F}{RT} c_{PF_6^-}(L, t) E(L, t) = 0. \quad [7.4]$$

The system of Eqs. 6 and 7 was developed in,¹ where it was solved under the electro-neutrality assumption. In this paper the electro-neutrality assumption is not applied. Instead, the Poisson equation describing the electric field in the electrolyte as a function of net charge density is considered. The Poisson equation (see,²⁰ Eq. 13.3.5)) has been represented by

$$\rho(y) = \epsilon \epsilon_0 \frac{\partial E}{\partial y}, \quad [8]$$

where $\rho(y)$ is the net charge density [C · m⁻³], ϵ_0 is the permittivity of free space, 8.85410 · 10⁻¹² C² · N⁻¹ · m⁻², and ϵ is the dielectric constant of the electrolyte. It has been reported that $\epsilon = 95$ for ethylene carbonate and $\epsilon = 64$ for propylene carbonate.^{20,21} Note that by definition

$$\rho(y, t) = F(c_{Li^+}(y, t) - c_{PF_6^-}(y, t)). \quad [9]$$

Eqs. 6-8 determine the concentration development of both ions in time and space.

According to Eq. 9, ρ is proportional to the difference between c_{Li^+} and $c_{PF_6^-}$, two quantities which are large in magnitude and close in value. This means ρ is calculated with large numerical errors. It is convenient to define the average concentration c and introduce the deviation in concentrations δ , according to

$$c(y, t) = (c_{Li^+}(y, t) + c_{PF_6^-}(y, t))/2, \quad [10.1]$$

$$\delta(y, t) = (c_{Li^+}(y, t) - c_{PF_6^-}(y, t))/2. \quad [10.2]$$

The inverse transformation gives

$$c_{Li^+}(y, t) = c(y, t) + \delta(y, t), \quad [11.1]$$

$$c_{PF_6^-}(y, t) = c(y, t) - \delta(y, t). \quad [11.2]$$

Note that c is the average salt concentration in the electrolyte and amounts to 1500 mol · m⁻³ for conventional Li-ion batteries. In contrast, the deviation δ is 8 to 10 orders of magnitude smaller as will be shown in the subsequent sections. Therefore transformation of Eqs. 10 separates the effects of different scales in the electrolyte. Eqs. 6 and 7 can now be rewritten in terms of the new variables c and δ . Eqs. 6 are therefore multiplied by $D_{PF_6^-}$ and Eqs. 7 by D_{Li^+} . Subsequently, Eqs. 6 and 7 are added and subtracted and Eqs. 11 are applied. This leads to

$$\frac{D_{Li^+} + D_{PF_6^-}}{2D_{PF_6^-}} \frac{\partial c}{\partial t} = D_{Li^+} \frac{\partial^2 c}{\partial y^2} - D_{Li^+} \frac{F}{RT} \frac{\partial (\delta E)}{\partial y} - \frac{D_{PF_6^-} - D_{Li^+}}{2D_{PF_6^-}} \frac{\partial \delta}{\partial t}, \quad [12.1]$$

$$c(y, 0) = c_0, \quad [12.2]$$

$$\frac{\partial c(0, t)}{\partial y} - \frac{F}{RT} \delta(0, t) E(0, t) = -\frac{I_{LiC_6}(t)}{2FAD_{Li^+}}, \quad [12.3]$$

$$\frac{\partial c(L, t)}{\partial y} - \frac{F}{RT} \delta(L, t) E(L, t) = \frac{I_{LiCoO_2}(t)}{2FAD_{Li^+}}, \quad [12.4]$$

and

$$\frac{D_{Li^+} + D_{PF_6^-}}{2D_{PF_6^-}} \frac{\partial \delta}{\partial t} = D_{Li^+} \frac{\partial^2 \delta}{\partial y^2} - D_{Li^+} \frac{F}{RT} \frac{\partial(cE)}{\partial y} - \frac{D_{PF_6^-} - D_{Li^+}}{2D_{PF_6^-}} \frac{\partial c}{\partial t}, \quad [13.1]$$

$$\delta(y, 0) = 0, \quad [13.2]$$

$$\frac{\partial \delta(0, t)}{\partial y} - \frac{F}{RT} c(0, t) E(0, t) = -\frac{I_{LiC_6}(t)}{2FAD_{Li^+}}, \quad [13.3]$$

$$\frac{\partial \delta(L, t)}{\partial y} - \frac{F}{RT} c(L, t) E(L, t) = \frac{I_{LiCoO_2}(t)}{2FAD_{Li^+}}. \quad [13.4]$$

Substituting Eq. 9 and Eq. 10.2 into Eq. 8, the Poisson equation can be rewritten as

$$\frac{\partial E}{\partial y} = \frac{2F}{\epsilon \epsilon_0} \delta. \quad [14]$$

Eqs. 12–14 give a general description of the development of concentration gradients inside battery electrolytes.

Steady-state condition.— Eqs. 12–14 describes the development of concentration gradients as a function of time when a current is flowing through the battery. These concentrations, in turn, determine the overvoltages across the electrolyte which characterize the energy and power losses due to mass and charge transport in the electrolyte.¹ The overvoltages reach a maximal value under steady-state conditions, when no changes in the electric field and concentration gradients are induced anymore. It is therefore to be expected that deviations from electro-neutrality should be maximal under steady-state conditions.

The mathematical implications of steady-state conditions will be further investigated in this section. Suppose that the applied current is constant ($I(t) = I$) and steady state is reached, obviously no changes in concentration profiles are observed and therefore all derivatives with respect to time (Eqs. 12.1 and 13.1) become zero. Eqs. 12.1, 13.1 and 14 then reduce to

$$\frac{\partial^2 c}{\partial y^2} = f \frac{\partial(\delta E)}{\partial y}, \quad [15]$$

$$\frac{\partial^2 \delta}{\partial y^2} = f \frac{\partial(cE)}{\partial y}, \quad [16]$$

$$\frac{\partial E}{\partial y} = \frac{2F}{\epsilon \epsilon_0} \delta, \quad [17]$$

respectively, where $f = F/(RT)$. As the steady state solution only depends on the space variable y , the partial derivatives can be replaced by ordinary derivatives. Since no side reactions are considered to take place in the present model, the constant current flowing through the battery (I) can be represented by $I = I_{LiCoO_2} = -I_{LiC_6}$. Integrating Eqs. 15 and 16, and taking into account the boundary conditions given in Eqs. 12.3–12.4 and 13.3–13.4 leads to

$$\frac{dc}{dy} - f \delta E = \frac{J_0}{2}, \quad [18]$$

$$\frac{d\delta}{dy} - f c E = \frac{J_0}{2}, \quad [19]$$

$$\frac{dE}{dy} = \frac{2F}{\epsilon \epsilon_0} \delta, \quad [20]$$

describing the diffusion-migration process under steady state, where $J_0 = I/(FAD_{Li^+})$. Note that Eqs. 18–20 are first order ordinary differential equations (ODEs) that must be solved with respect to one additional condition. One can specify the value for $c(0)$, though any other point between 0 and L can also be used. Alternatively, a normalization condition can be applied, however, the choice of this normalization condition is far from trivial. Indeed Eqs. 7.2–7.4 imply that

$$\int_0^L c_{PF_6^-}(y) dy = c_0 L, \quad [21]$$

since no net influx of PF_6^- ions into electrolyte can take place. A similar normalization condition for Li^+ ions can be given by

$$\int_0^L c_{Li^+}(y) dy = c_0 L(1 + 2\kappa). \quad [22]$$

If κ is equal to zero then the total charge of all ions in the electrolyte is zero. Re-parameterization of Eqs. 10–11 applied to Eq. 21–22 leads to

$$\int_0^L c(y) dy = c_0 L(1 + \kappa), \quad [23]$$

and

$$\int_0^L \delta(y) dy = c_0 L \kappa. \quad [24]$$

Therefore κ represents the ratio between the total excess concentration δ and the total equilibrium concentration of the salt in the electrolyte. Eqs. 21–22 determine the conservation law for anions and cations, respectively, and translate those limitations into the conditions for c and δ represented by Eqs. 23–24. However, the variable δ also represents, after multiplication by F , an electric charge, which gives the normalization condition for Eq. 20. Note that Eq. 20 and Eq. 24 jointly imply that

$$E(L) - E(0) = \frac{2F}{\epsilon \epsilon_0} \int_0^L \delta(y) dy = \kappa \frac{2Fc_0 L}{\epsilon \epsilon_0}. \quad [25]$$

From Eq. 25, the variable κ can be expressed via an increment in electric field into

$$\kappa = \frac{E(L) - E(0)}{\left(\frac{2Fc_0 L}{\epsilon \epsilon_0}\right)}. \quad [26]$$

Iterative solutions.— Eqs. 18–20 and normalization conditions given by Eqs. 23, 24 and 26 describe the steady-state concentrations in the electrolyte when no local or global electro-neutrality is assumed. This system of equations can be solved iteratively. Suppose that an initial guess for functions δ and E is available. Logically, the initial guess for δ is $\delta = 0$, which corresponds to the local electro-neutrality assumption, the Poisson equation then requires E to be constant. Therefore the normalization condition Eq. 24 (with κ defined by Eq. 26) immediately defines a value for parameter κ (i.e. $\kappa = 0$, global electro-neutrality). After that, Eq. 18 is solved together with the normalization condition given in Eq. 23. The solution is substituted into Eq. 19, from which the electric field E is derived. Furthermore, E is substituted into Eq. 20 which results in the readjusted net-charge density δ . Finally, Eq. 26 can be applied to readjust κ .

The process described above can be repeated many times, each time starting from δ and E obtained during the previous iteration.

Denoting the iteration number as n , the iterative process can then be formalized by the following set of indexed equations

$$\frac{dc^{(n+1)}}{dy} = f\delta^{(n)}E^{(n)} + J_0/2, \quad [27]$$

$$\int_0^L c^{(n+1)}(y)dy = c_0L(1 + \kappa^{(n)}), \quad [28]$$

$$E^{(n+1)} = \frac{1}{fc^{(n+1)}} \left[J_0/2 - \frac{d\delta^{(n)}}{dy} \right], \quad [29]$$

$$\delta^{(n+1)} = \frac{\varepsilon\varepsilon_0}{2F} \frac{dE^{(n+1)}}{dy}, \quad [30]$$

$$\kappa^{(n+1)} = \frac{E^{(n+1)}(L) - E^{(n+1)}(0)}{\left(\frac{2Fc_0L}{\varepsilon\varepsilon_0} \right)}. \quad [31]$$

Note that the left hand sides of equations Eqs. 27 and 29–31 determine the next $(n + 1)^{\text{th}}$ approximation to the final solution, taking the values determined in the previous n^{th} step as input values. Eq. 28 is a normalization condition necessary to solve Eq. 27. Apparently if the iterative process converges then it converges to the final solution

$$\frac{dc^{(\infty)}}{dy} = f\delta^{(\infty)}E^{(\infty)} + J_0/2, \quad [32]$$

$$\int_0^L c^{(\infty)}(y)dy = c_0L(1 + \kappa), \quad [33]$$

$$E^{(\infty)} = -\frac{1}{fc^{(\infty)}} \left[J_0/2 - \frac{d\delta^{(\infty)}}{dy} \right], \quad [34]$$

$$\delta^{(\infty)} = \frac{\varepsilon\varepsilon_0}{2F} \frac{dE^{(\infty)}}{dy}, \quad [35]$$

$$\kappa^{(\infty)} = \frac{E^{(\infty)}(L) - E^{(\infty)}(0)}{\left(\frac{2Fc_0L}{\varepsilon\varepsilon_0} \right)}, \quad [36]$$

which coincides with the solution of Eqs. 18–20, 23 and 26. Upon approaching convergence, one expects the difference between n^{th} and $(n + 1)^{\text{th}}$ iterations to become negligible.

Refinement of the iterative process.— Implementation of the iterative process (Eqs. 27–31) requires finding a solution of the ODE given in Eq. 27 with normalization condition Eq. 28, which requires another integration step. This integration step is nontrivial but can be performed analytically, therefore more accurate by the following re-parametrization. Consider the initial values (i.e. 0 step): $\delta^{(0)}(y) = 0$, $\kappa^{(0)} = 0$ and assume that $E^{(0)}(y)$ is equal to an arbitrary constant number. Then the first iteration step of the algorithm given by Eqs. 27–31 will correspond to a solution of steady-state equations based on electro-neutrality assumption, thus

$$c^{(1)}(y) = c_0 + (y - L/2)J_0/2, \quad [37]$$

$$E^{(1)}(y) = -\frac{1}{2f} \cdot \frac{J_0}{c_0 + (y - L/2)J_0/2}, \quad [38]$$

$$\delta^{(1)}(y) = \frac{J_0^2\varepsilon\varepsilon_0RT}{2F^2(2c_0 + (y - L/2)J_0)^2}, \quad [39]$$

$$\kappa^{(1)} = \frac{J_0^2\varepsilon\varepsilon_0}{8fFc_0} \cdot \frac{1}{c_0^2 - (J_0L/4)^2}. \quad [40]$$

Function $c^{(1)}(y)$ represents the average concentration of ions under local electro-neutrality conditions (see).¹ Consider re-parameterization of algorithm Eq. 27–31 in terms of function $\hat{c}^{(n)}(y)$ determined as

$$\hat{c}^{(n)}(y) = c^{(n)}(y) - c^{(1)}(y). \quad [41]$$

Apparently, the function $\hat{c}^{(n)}(y)$ is the difference between the n^{th} and the first iteration. This represents the difference between the corrected concentrations, calculated by the iterative algorithm, and the model assuming local electro-neutrality. Note that

$$\frac{dc^{(n+1)}}{dy} = \frac{d\hat{c}^{(n+1)}}{dy} + J_0/2 \quad \text{and} \quad \int_0^L c^{(n+1)}(y)dy = \int_0^L \hat{c}^{(n+1)}(y)dy + c_0L. \quad [42]$$

Taking Eqs. 41–42 into account, Eqs. 27–31 can be rewritten as

$$\frac{d\hat{c}^{(n+1)}}{dy} = f\delta^{(n)}E^{(n)}, \quad [43]$$

$$\int_0^L \hat{c}^{(n+1)}(y)dy = c_0L\kappa^{(n)}, \quad [44]$$

$$E^{(n+1)} = -\frac{1}{f(\hat{c}^{(n+1)} + c^{(1)})} \left[J_0/2 - \frac{d\delta^{(n)}}{dy} \right], \quad [45]$$

$$\delta^{(n+1)} = \frac{\varepsilon\varepsilon_0}{2F} \frac{dE^{(n+1)}}{dy}, \quad [46]$$

$$\kappa^{(n+1)} = \frac{E^{(n+1)}(L) - E^{(n+1)}(0)}{\left(\frac{2Fc_0L}{\varepsilon\varepsilon_0} \right)}. \quad [47]$$

Considering that $\delta^{(n)}E^{(n)} = \frac{\varepsilon\varepsilon_0}{2F}E^{(n)}\frac{dE^{(n)}}{dy} = \frac{\varepsilon\varepsilon_0}{4F}\frac{d(E^{(n)})^2}{dy}$ an explicit solution of Eq. 43 can be given. Indeed integrating both sides of Eq. 43 from zero to y results in

$$\begin{aligned} \hat{c}^{(n+1)}(y) &= \hat{c}^{(n+1)}(0) + f \int_0^y \delta^{(n)}E^{(n)}dy \\ &= \hat{c}^{(n+1)}(0) + \frac{\varepsilon\varepsilon_0}{4RT} [(E^{(n)}(y))^2 - (E^{(n)}(0))^2]. \end{aligned} \quad [48]$$

When Eq. 48 is substituted into the normalization condition of Eq. 44 it gives

$$c_0L\kappa^{(n)} = \hat{c}^{(n+1)}(0)L + \frac{\varepsilon\varepsilon_0}{4RT} \left[\int_0^L (E^{(n)}(y))^2 dy - (E^{(n)}(0))^2 L \right]. \quad [49]$$

From Eq. 49 the initial value $\hat{c}^{(n+1)}(0)$ can be analytically expressed as

$$\hat{c}^{(n+1)}(0) = \left\{ c_0\kappa^{(n)} - \frac{\varepsilon\varepsilon_0}{4RT} \left[\frac{1}{L} \int_0^L (E^{(n)}(y))^2 dy - (E^{(n)}(0))^2 \right] \right\}, \quad [50]$$

Figure 2. $c^{(1)}$ (curve (a)), $E^{(1)}$ (curve (b)) and $10^{10} \cdot \delta^{(1)}$ (curve (c)), as a function of distance y across the electrolyte. The left axis corresponds to concentrations $c^{(1)}$ and $\delta^{(1)}$, the right axis refers to the electric field $E^{(1)}$. Note the scaling factor in front of $\delta^{(1)}$.

and therefore function $\hat{c}^{(n+1)}(y)$ also has an analytical form

$$\begin{aligned} \hat{c}^{(n+1)}(y) &= \left\{ c_0 \kappa^{(n)} - \frac{\varepsilon \varepsilon_0}{4RT} \left[\frac{1}{L} \int_0^L (E^{(n)}(y))^2 dy - (E^{(n)}(0))^2 \right] \right\} \\ &\quad + \frac{\varepsilon \varepsilon_0}{4RT} [(E^{(n)}(y))^2 - (E^{(n)}(0))^2] \\ &= \left\{ c_0 \kappa^{(n)} - \frac{\varepsilon \varepsilon_0 F}{4RT L} \int_0^L (E^{(n)}(y))^2 dy \right\} + \frac{\varepsilon \varepsilon_0}{4RT} (E^{(n)}(y))^2. \end{aligned} \quad [51]$$

The final system of equations defining the iterative algorithm can be written in the following form

$$\hat{c}^{(n+1)}(y) = c_0 \kappa^{(n)} + \frac{\varepsilon \varepsilon_0}{4RT} \left\{ (E^{(n)}(y))^2 - \frac{1}{L} \int_0^L (E^{(n)}(y))^2 dy \right\}, \quad [52]$$

$$E^{(n+1)}(y) = -\frac{1}{f(\hat{c}^{(n+1)}(y) + c^{(1)}(y))} \left[J_0/2 - \frac{d\delta^{(n)}}{dy} \right], \quad [53]$$

$$\delta^{(n+1)}(y) = \frac{\varepsilon \varepsilon_0}{2F} \frac{dE^{(n+1)}}{dy}, \quad [54]$$

$$\kappa^{(n+1)} = \frac{E^{(n)}(L) - E^{(n)}(0)}{\left(\frac{2Fc_0L}{\varepsilon \varepsilon_0} \right)}, \quad [55]$$

where the starting values for $n = 1$ are given by Eqs. 37–40. This iterative algorithm consists only of four explicit equations and contains no other normalization conditions. The iterative procedure Eqs. 52–55 was implemented using the Symbolic Toolbox in Matlab. That implementation was chosen to reduce an error accumulation which is present in cases when iterations are performed numerically, i.e. with finite accuracy.

Results and Discussion

First iteration.— Simulations described in this section are performed with parameter values $D_{Li^+} = 2 \cdot 10^{-11} \text{ m}^2 \cdot \text{s}^{-1}$, $A = 0.02 \text{ m}^2$,

$L = 2.8 \cdot 10^{-4} \text{ m}$, $c_0 = 1500 \text{ mol} \cdot \text{m}^{-3}$ and $I = 0.72 \text{ A}$, which corresponds to the case of typical fully charged Li-ion batteries.²¹ As explained in the previous sections, the first iteration of the iterative process (Eq. 37–40) produces the set of $c^{(1)}(y)$, $\delta^{(1)}(y)$, $E^{(1)}(y)$, and $\kappa^{(1)}$. These functions and parameter represent the average concentration, the local deviation from electro-neutrality, the electric field and the global deviation from electro-neutrality, respectively. Fig. 2 illustrates the results obtained for $c^{(1)}$, $\delta^{(1)}$ and $E^{(1)}$. Note the difference in magnitude between c and δ (left vertical scale). As Fig. 2 shows, the average concentration is a linear function of the space variable y . It is small near the interface of the negative electrode and large at the positive electrode, where it reaches a magnitude of $2800 \text{ mol} \cdot \text{m}^{-3}$. In contrast, δ is about 10 orders of magnitude smaller, and is largest near the negative electrode, quickly decaying to zero when y increases. It is interesting to note that δ is positive, indicating excess of Li^+ ions in the solution under steady-state. The deviation from electro-neutrality δ is quite small; however, it is sufficient to induce a considerable electric field (right-hand axis), which is not surprising as the F/ε_0 pre-factor in the Poisson equation has an order of magnitude of 10^{16} . Fig. 2 shows that the electric field reaches a maximum near the negative electrode upon charging, at the same location where deviation from electro-neutrality is largest. Similar figures are obtained for the subsequent iterations for $c^{(i)}$, $\delta^{(i)}$ and $E^{(i)}$, $i = 2, 3$ but those plots will be visually the same, because the absolute difference between the function after two consecutive iterations is much smaller than the function value itself. This difference is several orders of magnitude smaller than the actual value, which will be discussed in the next section.

Higher order iterations.— One of the key questions for the derived iterative algorithm is to decide whether convergence is achieved. One of the commonly accepted criteria for that is to check the difference in values of the target functions after two consecutive iterations. If this difference is small, then convergence is accomplished. In this section the convergence of the iterative process is investigated for the parameters D_{Li^+} , A , L , c_0 and I . To illustrate the convergence rate the differences between the subsequent iterations $c^{(1)}(y) - c^{(0)}(y)$, $c^{(2)}(y) - c^{(1)}(y)$ and $c^{(3)}(y) - c^{(2)}(y)$ are plotted in Fig. 3. It can be seen that $c^{(1)}(y) - c^{(0)}(y)$ and $c^{(2)}(y) - c^{(1)}(y)$ differ about 9 orders of magnitude. $c^{(3)}(y) - c^{(2)}(y)$ demonstrates another 9 orders of magnitude decrease. Therefore it can be concluded that for the considered set of parameters convergence is effectively achieved already after the first iteration step. The second and the third iterations reveal only minor corrections.

Figure 3. Increments between two consecutive iterations $c^{(i)} - c^{(i-1)}$, $i = 1, 2, 3$. Curve (a) corresponds to $c^{(1)} - c^{(0)}$; curve (b) corresponds to $5 \cdot 10^9 \cdot (c^{(2)} - c^{(1)})$; curve (c) corresponds to $2 \cdot 10^{18} \cdot (c^{(3)} - c^{(2)})$. Note the scaling factors for curves (b) and (c).

Differences in the electric field are shown in Fig. 4. Again, convergence is very fast and the correction after each iteration declines several orders of magnitude. Note that $E^{(3)}(y) - E^{(2)}(y)$ clearly demonstrates random numerical noise, indicating that the difference between the second and third iteration is so small that it cannot be properly computed within MATLAB double precision arithmetic (complied with IEEE Standard 754). Fig. 5 shows the simulation results of $\delta^{(i)}(y) - \delta^{(i-1)}(y)$. Like in the case of the electric field, final convergence is reached after 3 iterations, which becomes clear from the random numerical noise.

Current dependence.— All simulations in the previous sections were performed with a fixed current $I = 0.72$ A. However, it is well known that the electric field in the electrolyte depends on the applied current. It is therefore of interest to investigate how the solution obtained from the iterative algorithm behaves as a function of the applied current. Note that I enters into the solution only via $J_0 = I/(FAD_{Li+})$, where J_0 is a steady-state flux [$\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$] at the

Figure 4. Incremental plots for $E^{(i)} - E^{(i-1)}$, $i = 1, 2, 3$. Curve (a) corresponds to $E^{(1)}$; curve (b) corresponds to $5 \cdot 10^8 \cdot (E^{(2)} - E^{(1)})$; curve (c) corresponds to $2 \cdot 10^{14} \cdot (E^{(3)} - E^{(2)})$. Note the scaling factors for curves (b) and (c).

Figure 5. Incremental plots for $\delta^{(i)} - \delta^{(i-1)}$, $i = 1, 2, 3$. Curve (a) corresponds to $\delta^{(1)} - \delta^{(0)}$; curve (b) corresponds to $10^9 \cdot (\delta^{(2)} - \delta^{(1)})$; curve (c) corresponds to $10^{14} \cdot (\delta^{(3)} - \delta^{(2)})$. Note the scaling factors for curves (b) and (c).

electrode interfaces. For this reason the dependence of the solution is investigated with respect to J_0 . In the subsequent simulations J_0 is varied between 0 and $J_{\text{lim}} = 4c_0/L$. The latter value corresponds to the limiting flux, when the average concentration c at $x = 0$ reaches 0. Apparently this flux corresponds to the maximal current that can pass the electrolyte. The used step-size of the J_0/J_{lim} grid is 0.0001 up to 0.9999 J_{lim} .

The maximum values for E and δ after the first iteration can be found at $x = 0$, as suggested by their expressions and Fig. 2. Curve (a) in Fig. 6 illustrates the dependence of δ_{max} as a function of the normalized flux. Curve (b) in Fig. 6 represents the average deviation from electro-neutrality across the electrolyte

$$\langle \delta \rangle = \frac{1}{L} \int_0^L \delta(y) dy = c_0 \kappa. \quad [56]$$

Figure 6. (a) Average value of deviation from the electro-neutrality ($\langle \delta \rangle$) and (b) the maximum value (δ_{max}) across the electrolyte as a function of the normalized current upon charging.

Figure 7. (a) Absolute magnitude of the maximum electric field (E_{max}) and (b) the average electric field ($\Delta\phi/L$) as a function of the normalized current upon charging.

Note that $\langle\delta\rangle/c_0 = \kappa$, thus $\langle\delta\rangle$ represents the global deviation from electro-neutrality in terms of concentration. In contrast, the parameter κ represents the global deviation from electro-neutrality in relative terms. It can be seen that for small currents both $\langle\delta\rangle$ and δ_{max} are close in magnitude, while for large currents those two functions can differ several orders of magnitude. That indicates a strong local deviation from electro-neutrality at the places with high electric fields, i.e. near $x = 0$ during charging. It is also clearly visible that $\langle\delta\rangle$ and δ_{max} grow with the flux, however even for near-limiting currents, both $\langle\delta\rangle$ and δ_{max} are far below $1 \text{ mol} \cdot \text{m}^{-3}$ which is extremely small for conventional Li-ion batteries. Average deviations from electro-neutrality evaluated after the first iteration can also be found analytically

$$\langle\delta\rangle^{(1)} = \frac{J_0^2 \epsilon \epsilon_0}{8fF} \cdot \frac{1}{c_0^2 - (J_0 L/4)^2}, \quad [57]$$

which is comparable to Eq. 40.

Fig. 7 illustrates the behavior of the electric field E after the first iteration. The maximum value of the amplitude of electric field $|E_{max}|$ and the average electric field $\langle E \rangle$ across the electrolyte layer are plotted. Note that the average electric field across the electrolyte is proportional to the migration potential drop according to

$$\langle E \rangle = \frac{1}{L} \int_0^L E(y) dy = \frac{\Delta\phi}{L}. \quad [58]$$

In general, the shape of the curves in Fig. 7 are very similar to those shown in Fig. 6, one can see that the potential drop evolves less sharply than the maximum electric field near the limiting flux. That can be explained by the fact that the potential drop is an integral of the electric field and must therefore be smoother.

The square dots in Figs. 6 and 7 correspond to a current of $I = 0.72 \text{ A}$ used in the previous sections.

Dependence on the current and salt concentration.— The results described in the previous sections imply that for practically relevant currents, the deviation from electro-neutrality in Li-ion batteries is small and can be reliably determined on the basis of the first iteration of the algorithm represented by Eqs. 37–40. However, the situation changes significantly when the equilibrium concentration c_0 declines. Fig. 8 shows the deviation from electro-neutrality (κ) as function of the normalized applied current/flux (J/J_0) and the total ionic concentration c_0 . The variables κ and c_0 are both given on a logarithmic scale. The range of interest for c_0 is from 10^{-3} to $10^4 \text{ mol} \cdot \text{m}^{-3}$.

Figure 8. Calculated $\log \kappa$ after 5 iterations as a function of average concentration ($\log c_0$) and applied flux (J/J_{lim}).

Like in the previous sections the applied current/flux ranges from $0 \leq J \leq J_{lim}$, normalized to J_{lim} . κ is obtained after five consecutive iterations. Five iterations are applied here because of the slower convergence at lower values of c_0 . Two main observations can be made. Firstly, deviation from electro-neutrality increases with increasing current for all c_0 . Secondly, deviation from electro-neutrality systematically increases with decreasing c_0 . Therefore, deviation from electro-neutrality can be large in electrochemical systems with low salt concentrations (see).^{22–25} For highly-concentrated solutions the Debye length is in nanometer range, whereas for low concentration electrolytes it can be micrometers thick, therefore Poisson-Nernst-Planck approach is less accurate. In case of Li-ion batteries, however, the Debye length is below 1 nm, thus the distortion from electro-neutrality caused by electrical double layers occur in less than 0.02% of total electrolyte thickness. At the same time, the relative deviation from electro-neutrality is only of order $10^{-7}\%$ which is extremely small, but present across whole bulk of the solution. This case is illustrated in Fig. 8 by the black lines representing typical concentration and current levels for Li-ion batteries.

Conclusions

The influence of the electro-neutrality assumption in Li-ion battery electrolytes has been mathematically investigated. A general system of equations, describing the development of concentration gradients in simple binary electrolytes is considered. A rearrangement of standard Nernst-Planck equations in terms of average concentration and deviation from the average concentration is applied to improve accuracy. A universal iterative method under steady-state (dis)charging conditions is proposed. This iterative process devised for solving the present system of equations in absence of electro-neutrality is simple, converges fast and can easily be generalized for the case of complex 3D (porous) electrolyte systems.²⁶ For the specific case of steady-state conditions, the deviation from electro-neutrality has been evaluated. It was found that in the case of Li-ion batteries the deviation from electro-neutrality in terms of ionic concentrations is small and does generally not exceed $10^{-7}\%$. This result is also in line with the measured steady-state concentration gradients.¹⁹ However the deviation from electro-neutrality can be considerably larger when near-limiting currents are applied to the battery, which leads to large electric fields. The presented results also explain why the electro-neutrality assumption is so successful. The electro-neutral solution is proven to be the first iteration in sequence of approximations which lead to a general solution. Modeling studies, employing the electro-neutrality assumption for Li-ion batteries, therefore usually provide accurate and physically

meaningful solutions due to fast convergence of the iterative process. However, several subsequent iterations should be taken into account to check convergence or improve accuracy of approximation when necessary.

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