



Li-ion electrolyte modeling: The impact of adding supportive salts

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ARTICLE INFO

Article history:

Received 31 July 2008

Accepted 10 September 2008

Available online 24 September 2008

Keywords:

Li-ion battery

Electrolyte modeling

ABSTRACT

In recent work the ionic transportation properties of organic electrolyte in Li-ion batteries has been described in detail by the present authors, taking into account ionic diffusion and migration processes. Advanced battery electrolytes may, however, be composed of various salts. Therefore the ionic transport properties of such complex electrolytes have been investigated from a theoretical point of view. Detailed information about transient and steady-state behavior of the electrolyte has been simulated, including potential gradients and the diffusion and migration fluxes for all ions. It was found that supportive electrolytes are an effective way to reduce the electric field and, consequently, the migration overpotential. Simultaneously, the diffusion overpotential, in general, increases. Nevertheless, supportive salts reduce the total overpotential across the electrolyte, especially when high currents are applied for short periods of time.

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1. Introduction

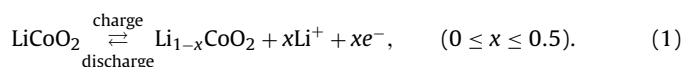
Improving the properties of advanced Li-ion batteries is challenging and a requirement for high power applications. It has been reported that the electrolyte of Li-ion batteries is responsible for substantial energy losses, especially under high current (dis)charging conditions [1]. The reason for these losses is the limited ionic conductivity of the non-aqueous Li-salt containing electrolytes.

Mathematical modeling is traditionally used to investigate the performance of rechargeable batteries [2–4]. In the case of Li-ion batteries the ionic transportation properties of the organic electrolyte has been described in detail, taking into account diffusion and migration processes [4]. In recent work the present authors have provided a detailed analysis of the various overpotential contributions based on single salt electrolytes [5]. It is, however, known that advanced electrolytes are often composed of various salt components. The theoretical investigation of this specific and more complex case is described in the present work.

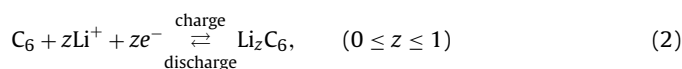
A mathematical model describing multi-component salt containing Li-ion electrolytes is proposed. The model consists of four coupled parabolic-type Partial Differential Equations (PDE's). A practically important question of how to improve the ionic conductivity properties of Li-based electrolytes is considered. It is found that adding supportive salts is an efficient way to reduce the electric field and, consequently, the overpotential.

2. Theoretical set-up

The elementary processes, occurring inside a conventional Li-ion battery, are schematically shown in Fig. 1. The main electrochemical storage reactions at the LiCoO_2 electrode can be represented by



describing the extraction of Li-ions from the positive electrode during charging and the insertion of Li^+ ions during discharging. The corresponding reactions at the negative electrode can be described by



As a result of these electrochemical charge transfer reactions, Li-ions must cross the electrolyte under current flowing conditions (see Fig. 1). The electrolyte in Li-ion batteries is based on a dissociated Li-salt, e.g. LiPF_6 or LiClO_4 , which cannot be considered as a well ionic-conductive medium. The ions in the electrolyte are transported by both diffusion and migration, this latter process being induced by the electric field between the electrodes across the electrolyte.

Consider that a conventional electrolyte is composed of a single salt, e.g. LiPF_6 . An interesting question is whether its properties can be improved by adding a “neutral salt” which does not affect the main electrochemical storage reactions. Consider the situation that another 1 M neutral salt, such as KClO_4 , is added to the standard

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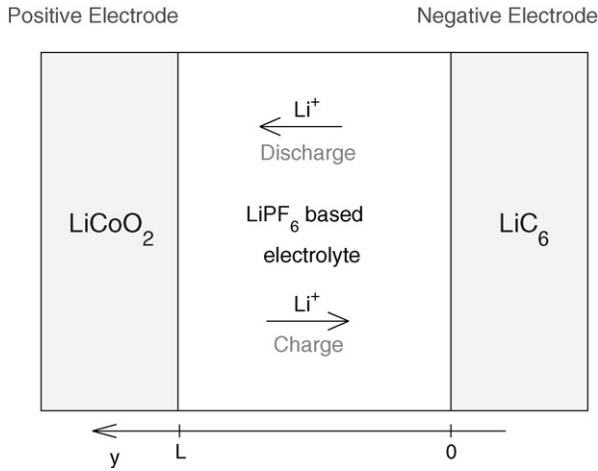


Fig. 1. Schematic representation of a conventional Li-ion battery, indicating the movements of Li-ions inside the electrolyte during charge and discharge.

electrolyte consisting of 1.5M LiPF₆. Denote the initial concentration of Li⁺ and PF₆⁻ as $c_{\text{Li}^+}^0$ and $c_{\text{PF}_6^-}^0$, respectively, where $c_{\text{Li}^+}^0 = c_{\text{PF}_6^-}^0$ and the initial concentration of K⁺ and ClO₄⁻ as $c_{\text{K}^+}^0$ and $c_{\text{ClO}_4^-}^0$, respectively, with $c_{\text{K}^+}^0 = c_{\text{ClO}_4^-}^0$. Furthermore, $c_0 = c_{\text{Li}^+}^0 + c_{\text{K}^+}^0 = c_{\text{PF}_6^-}^0 + c_{\text{ClO}_4^-}^0$.

The coordinate in Fig. 1 is defined from right to left and the position of the negative electrode/electrolyte interface is at $y=0$ and that of the positive electrode interface at $y=L$. The Nernst–Planck equation [6] relates the flux of all charged species in the electrolyte, according to

$$J_j = -D_j \frac{\partial c_j}{\partial y} - \frac{z_j F}{RT} D_j c_j \frac{\partial \phi}{\partial y}, \quad (3)$$

where $J_j(y,t)$ is the flux of species j [mol m² s] at position y at any moment of time t , D_j is the diffusion coefficient of j [m² s⁻¹], $\partial c_j / \partial y$ the concentration gradient [mol m⁻⁴], $\partial \phi / \partial y$ the potential gradient [V m⁻¹] and z_j is the valence state of j with $j = \text{Li}^+$ or PF₆⁻ in the case of a dissociated LiPF₆ salt. Herewith it is assumed that no convection takes place inside the electrolyte. Since, by definition the electric field $E(y,t) = \partial \phi(y,t) / \partial y$, $-E(y,t)$ will be further used in this paper instead of $\partial \phi / \partial y$.

The combined diffusion–migration process can be described by the following system of partial differential equations (PDE's)

$$\frac{\partial c_{\text{Li}^+}}{\partial t} = -\frac{\partial J_{\text{Li}^+}}{\partial y}, \quad (4.1)$$

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

$$J_{\text{Li}^+}(0, t) = -\frac{I_{\text{LiC}_6}(t)}{z_{\text{Li}^+} F A}, \quad (4.3)$$

$$J_{\text{Li}^+}(L, t) = \frac{I_{\text{LiCoO}_2}(t)}{z_{\text{Li}^+} F A}, \quad (4.4)$$

$$\frac{\partial c_{\text{K}^+}}{\partial t} = -\frac{\partial J_{\text{K}^+}}{\partial y}, \quad (5.1)$$

$$c_{\text{K}^+}(y, 0) = c_{\text{K}^+}^0, \quad (5.2)$$

$$J_{\text{K}^+}(0, t) = 0, \quad (5.3)$$

$$J_{\text{K}^+}(L, t) = 0, \quad (5.4)$$

and

$$\frac{\partial c_{\text{PF}_6^-}}{\partial t} = -\frac{\partial J_{\text{PF}_6^-}}{\partial y}, \quad (6.1)$$

$$c_{\text{PF}_6^-}(y, 0) = c_{\text{PF}_6^-}^0, \quad (6.2)$$

$$J_{\text{PF}_6^-}(0, t) = 0, \quad (6.3)$$

$$J_{\text{PF}_6^-}(L, t) = 0, \quad (6.4)$$

$$\frac{\partial c_{\text{ClO}_4^-}}{\partial t} = -\frac{\partial J_{\text{ClO}_4^-}}{\partial y}, \quad (7.1)$$

$$c_{\text{ClO}_4^-}(y, 0) = c_{\text{ClO}_4^-}^0, \quad (7.2)$$

$$J_{\text{ClO}_4^-}(0, t) = 0, \quad (7.3)$$

$$J_{\text{ClO}_4^-}(L, t) = 0, \quad (7.4)$$

where Eqs. (x.1), where index x runs from 4 to 7, represent the mass balances, Eqs. (x.2) reflect the fact that initially at $t=0$ no concentration profiles have been developed yet and hence that the concentrations across the electrolyte can be considered constant (c_0). Eqs. (4.3), (4.4) and Eqs. (5.3), (5.4) represent the flux conditions of Li⁺ and K⁺ ions, respectively, at both electrode/electrolyte interfaces. Corresponding flux conditions for anions are given by Eqs. (6.3), (6.4) and (7.3), (7.4). 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. Since no side reactions are considered to take place in the present model, the current flowing through the battery (I) can be represented by $I(t) = -I_{\text{LiCoO}_2}(t) = I_{\text{LiC}_6}(t)$. Obviously, for discharging the current definitions are reversed.

3. Overpotentials

The concentration and electric field gradients in the electrolyte result in electrochemical potential gradients. The electrochemical potential of Li⁺ ions ($\bar{\mu}_{\text{Li}^+}$ [J mol⁻¹]) is defined as

$$\bar{\mu}_{\text{Li}^+} = \mu_{\text{Li}^+}^0 + RT \ln \left(\frac{c_{\text{Li}^+}}{c_{\text{Li}^+}^{\text{ref}}} \right) + z_{\text{Li}^+} F \phi, \quad (8)$$

where $\mu_{\text{Li}^+}^0$ is the standard chemical potential, ϕ the electrostatic potential and $c_{\text{Li}^+}^{\text{ref}}$ is the reference concentration of 1 molar for Li⁺ ions. The difference in electrochemical potentials between both electrode/electrolyte interfaces represents the concentration polarization across the electrolyte, according to

$$\begin{aligned} \eta(t) &= \frac{1}{z_{\text{Li}^+} F} [\bar{\mu}_{\text{Li}^+}(L, t) - \bar{\mu}_{\text{Li}^+}(0, t)] \\ &= \frac{RT}{F} \ln \left(\frac{c_{\text{Li}^+}(L, t)}{c_{\text{Li}^+}(0, t)} \right) + (\phi(L, t) - \phi(0, t)), \end{aligned} \quad (9)$$

This overpotential is solely attributed to the transport limitations of the electrolyte and excludes the overpotential contributions of both charge transfer reactions. By definition

$$\phi(y, t) = \int_0^y \frac{\partial \phi}{\partial y}(y, t) dy = - \int_0^y E(y, t) dy, \quad (10)$$

where $E(y, t)$ is obtained by numerical solution of Eqs. (4.1)–(7.4), thus

$$\phi(L, t) - \phi(0, t) = - \int_0^L E(y, t) dy. \quad (11)$$

Consequently, $\eta(t)$ can be obtained at any moment of time, according to

$$\eta(t) = \frac{RT}{F} \ln \left(\frac{c(L, t)}{c(0, t)} \right) - \int_0^L E(y, t) dy. \quad (12)$$

4. Results and discussions

Consider first the steady-state situation, where the theoretical derivations are relatively simple. The ionic currents for each type of ions can be defined by

$$I_j = -z_j F A J_j, \quad (13)$$

where the fluxes are given by Eq. (3) and the development of all fluxes and concentrations is determined from Eqs. (4.1)–(7.4). By definition I at any location in the electrolyte of a Li-ion battery consists of contributions from all species and can, therefore, be expressed by

$$I = I_{\text{Li}^+}^d + I_{\text{PF}_6^-}^d + I_{\text{Li}^+}^m + I_{\text{PF}_6^-}^m + I_{\text{K}^+}^d + I_{\text{ClO}_4^-}^d + I_{\text{K}^+}^m + I_{\text{ClO}_4^-}^m, \quad (14)$$

where the diffusion-related currents carried by Li^+ and K^+ cations can be represented by

$$I_{\text{Li}^+}^d = z_{\text{Li}^+} F A D_{\text{Li}^+} \frac{\partial c_{\text{Li}^+}}{\partial y} = F A D_{\text{Li}^+} \frac{\partial c_{\text{Li}^+}}{\partial y}, \quad (15)$$

$$I_{\text{K}^+}^d = z_{\text{K}^+} F A D_{\text{K}^+} \frac{\partial c_{\text{K}^+}}{\partial y} = F A D_{\text{K}^+} \frac{\partial c_{\text{K}^+}}{\partial y}, \quad (16)$$

respectively. Similarly, the diffusion-related current of PF_6^- and ClO_4^- anions are given by

$$I_{\text{PF}_6^-}^d = z_{\text{PF}_6^-} F A D_{\text{PF}_6^-} \frac{\partial c_{\text{PF}_6^-}}{\partial y} = -F A D_{\text{PF}_6^-} \frac{\partial c_{\text{PF}_6^-}}{\partial y}, \quad (17)$$

$$I_{\text{ClO}_4^-}^d = z_{\text{ClO}_4^-} F A D_{\text{ClO}_4^-} \frac{\partial c_{\text{ClO}_4^-}}{\partial y} = -F A D_{\text{ClO}_4^-} \frac{\partial c_{\text{ClO}_4^-}}{\partial y}, \quad (18)$$

respectively. The migration-related currents of cations and anions can be represented by

$$I_{\text{Li}^+}^m = -\frac{z_{\text{Li}^+}^2 F^2 A D_{\text{Li}^+} c_{\text{Li}^+}}{RT} \cdot E = -\frac{F^2 A D_{\text{Li}^+} c_{\text{Li}^+}}{RT} \cdot E, \quad (19)$$

$$I_{\text{K}^+}^m = -\frac{z_{\text{K}^+}^2 F^2 A D_{\text{K}^+} c_{\text{K}^+}}{RT} \cdot E = -\frac{F^2 A D_{\text{K}^+} c_{\text{K}^+}}{RT} \cdot E, \quad (20)$$

and

$$I_{\text{PF}_6^-}^m = -\frac{z_{\text{PF}_6^-}^2 F^2 A D_{\text{PF}_6^-} c_{\text{PF}_6^-}}{RT} \cdot E = -\frac{F^2 A D_{\text{PF}_6^-} c_{\text{PF}_6^-}}{RT} \cdot E, \quad (21)$$

$$I_{\text{ClO}_4^-}^m = -\frac{z_{\text{ClO}_4^-}^2 F^2 A D_{\text{ClO}_4^-} c_{\text{ClO}_4^-}}{RT} \cdot E = -\frac{F^2 A D_{\text{ClO}_4^-} c_{\text{ClO}_4^-}}{RT} \cdot E. \quad (22)$$

Since Li^+ cations are the only charge carrying ions during battery operation, the following conditions must hold under steady-state

$$I_{\text{Li}^+}^d + I_{\text{Li}^+}^m = I, \quad (23)$$

$$I_{\text{K}^+}^d + I_{\text{K}^+}^m = 0, \quad (24)$$

$$I_{\text{PF}_6^-}^d + I_{\text{PF}_6^-}^m = 0, \quad (25)$$

$$I_{\text{ClO}_4^-}^d + I_{\text{ClO}_4^-}^m = 0. \quad (26)$$

Performing trivial substitutions the following expressions are obtained

$$\frac{\partial c_{\text{Li}^+}}{\partial y} - \frac{F}{RT} c_{\text{Li}^+} E = \frac{I}{F A D_{\text{Li}^+}}, \quad (27)$$

$$\frac{\partial c_{\text{K}^+}}{\partial y} - \frac{F}{RT} c_{\text{K}^+} E = 0, \quad (28)$$

$$\frac{\partial c_{\text{PF}_6^-}}{\partial y} + \frac{F}{RT} c_{\text{PF}_6^-} E = 0, \quad (29)$$

$$\frac{\partial c_{\text{ClO}_4^-}}{\partial y} + \frac{F}{RT} c_{\text{ClO}_4^-} E = 0. \quad (30)$$

Defining the total concentrations of cations and anions as

$$c_+ = c_{\text{Li}^+} + c_{\text{K}^+} \quad \text{and} \quad c_- = c_{\text{PF}_6^-} + c_{\text{ClO}_4^-}. \quad (31)$$

and adding Eq. (27) to Eq. (28) and Eq. (29) to Eq. (30), this results in

$$\frac{\partial c_+}{\partial y} - \frac{F}{RT} c_+ E = \frac{I}{F A D_{\text{Li}^+}}, \quad (32)$$

$$\frac{\partial c_-}{\partial y} + \frac{F}{RT} c_- E = 0. \quad (33)$$

Furthermore, when electroneutrality is assumed

$$c_+ = c_- = c, \quad (34)$$

where c denotes the total concentration of charged species under electroneutrality conditions. Substituting Eq. (34) into Eqs. (32) and (33) leads to

$$\frac{\partial c}{\partial y} - \frac{F}{RT} c E = \frac{I}{F A D_{\text{Li}^+}}, \quad (35)$$

and

$$\frac{\partial c}{\partial y} + \frac{F}{RT} c E = 0. \quad (36)$$

From Eqs. (35) and (36) it follows that

$$\frac{\partial c}{\partial y} = \frac{I}{2 F A D_{\text{Li}^+}}. \quad (37)$$

The following conclusions can be drawn from these derivations. In the steady-state the total concentration profile in the electrolyte is linear and its steepness is determined only by the current density and the diffusion coefficient of Li^+ cations (D_{Li^+}). Indeed considering that $c_0 = c_{\text{Li}^+}^0 + c_{\text{K}^+}^0 = c_{\text{PF}_6^-}^0 + c_{\text{ClO}_4^-}^0$, the steady-state concentration profile is given by

$$c(y) = \frac{I}{2 F A D_{\text{Li}^+}} \left(y - \frac{L}{2} \right) + c_0. \quad (38)$$

From Eqs. (36) and (37) it follows that the electric field under steady-state conditions is

$$E(y) = -\frac{RT}{2 F^2 A D_{\text{Li}^+}} \frac{I}{c(y)}, \quad (39)$$

where $c(y)$ can be described by Eq. (38). Now it becomes possible to find not only the total concentration profiles but also those of the individual components. For example, c_{K^+} can be obtained by substituting Eq. (39) into Eq. (28), according to

$$\frac{\partial c_{\text{K}^+}}{\partial y} - \frac{F}{RT} c_{\text{K}^+} E = \frac{\partial c_{\text{K}^+}}{\partial y} + \frac{1}{2 F A D_{\text{Li}^+}} \frac{I}{c(y)} c_{\text{K}^+} = 0. \quad (40)$$

Since there is only one space variable (y) we may write the usual derivatives and obtain an ordinary differential equation (ODE), which has the following solution

$$c_{\text{K}^+}(y) = \frac{c_{\text{K}^+}^0 L}{\ln \left(\frac{c_0 + 4 F A D_{\text{Li}^+}}{c_0 - 4 F A D_{\text{Li}^+}} \right)} \cdot \frac{1}{y - \frac{L}{2} + \frac{2 c_0 F A D_{\text{Li}^+}}{I}}, \quad (41)$$

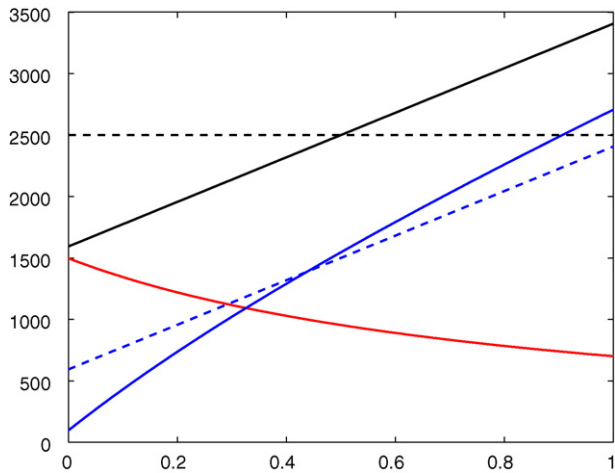


Fig. 2. Steady-state concentration profiles—black solid line: total concentration $c(y)$, black dashed line: c_0 , red solid line: $c_{K^+}(y)$, blue solid line: $c_{Li^+}(y)$, blue dashed line: $c_{Li^+}(y)$ for case without neutral salt. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

Note that a similar normalization condition has been used before [5]. After obtaining Eq. (41), $c_{Li^+}(y)$ is determined from $c_{Li^+}(y) = c(y) - c_{K^+}(y)$, where $c(y)$ is given by Eq. (38).

The results calculated under steady-state conditions are visualized in Fig. 2. The used simulation parameters are: electrolyte thickness $L = 2.8 \times 10^{-4}$ [m], surface area $A = 2 \times 10^{-2}$ [m²], constant current $I = 0.5$ [A] and $D_{Li^+} = 2 \times 10^{-11}$ [m²·s⁻¹]. The solid black line in Fig. 2 shows the total concentration profile of all cations $c(y)$. The red line represents $c_{Li^+}(y)$ and the blue line $c_{K^+}(y)$. The black dashed line shows the total initial concentrations of all cations c_0 . The blue dashed line indicates the steady-state concentration of Li⁺ ions for the case when no supporting salt is present in the electrolyte. It can clearly be seen that the concentration profile for the inert K⁺ has a slope opposite to that of Li⁺ under steady-state conditions. It is also clear that the gradient for K⁺ is smaller than that of Li⁺ as the result of the lower initial concentration. Under steady-state, the concentration profiles of both cations in the electrolyte are non-linear. $c_{PF_6^-}$ and $c_{ClO_4^-}$ can be obtained by solving Eqs. (29) and (30), using the appropriate normalization conditions. Indeed, from Eqs. (29) and

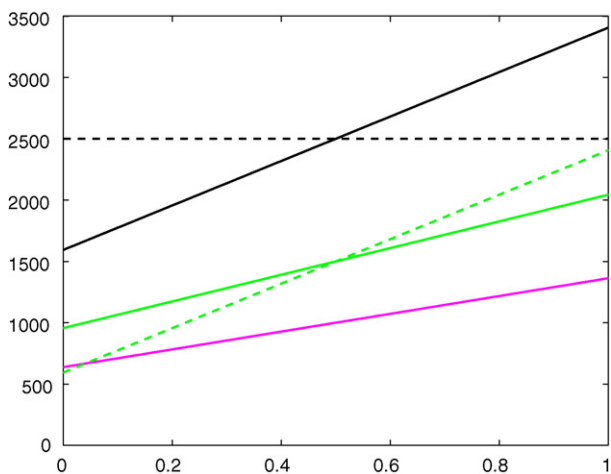


Fig. 3. Steady-state concentration profiles—black solid line: total concentration $c(y)$, black dashed line: c_0 , pink solid line: $c_{ClO_4^-}(y)$, green solid line: $c_{PF_6^-}(y)$, green dashed line: $c_{PF_6^-}(y)$ for case without neutral salt. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

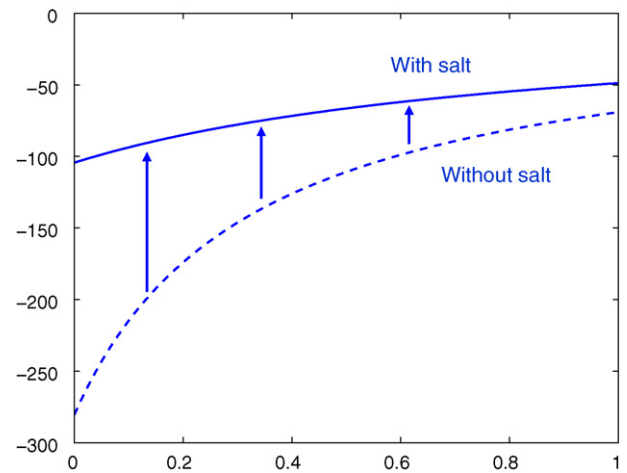


Fig. 4. Reduction in the steady-state electric field when support salt is added.

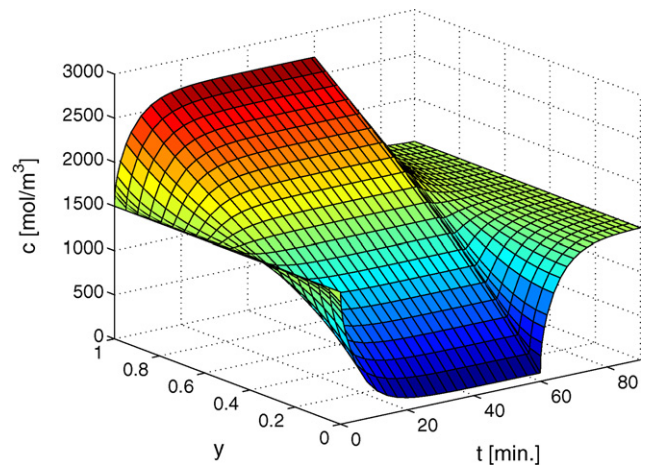


Fig. 5. Development of the total ionic concentration profile $c(y,t)$ inside the electrolyte, during constant current charging (0.5 [A]) and relaxation upon current interruption after 1 h.

(30) it follows that

$$\frac{\partial c_{PF_6^-}}{\partial y} + \frac{F}{RT} c_{PF_6^-} E = \frac{\partial c_{PF_6^-}}{\partial y} - \frac{1}{2FAD_{Li^+}} \frac{I}{c(y)} c_{PF_6^-} = 0, \quad (42)$$

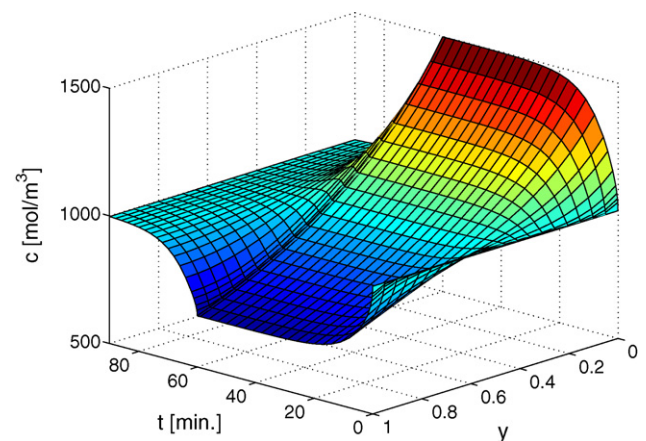


Fig. 6. Development of the K⁺ concentration profile $c_{K^+}(y,t)$ inside the electrolyte, under the same conditions as in Fig. 5.

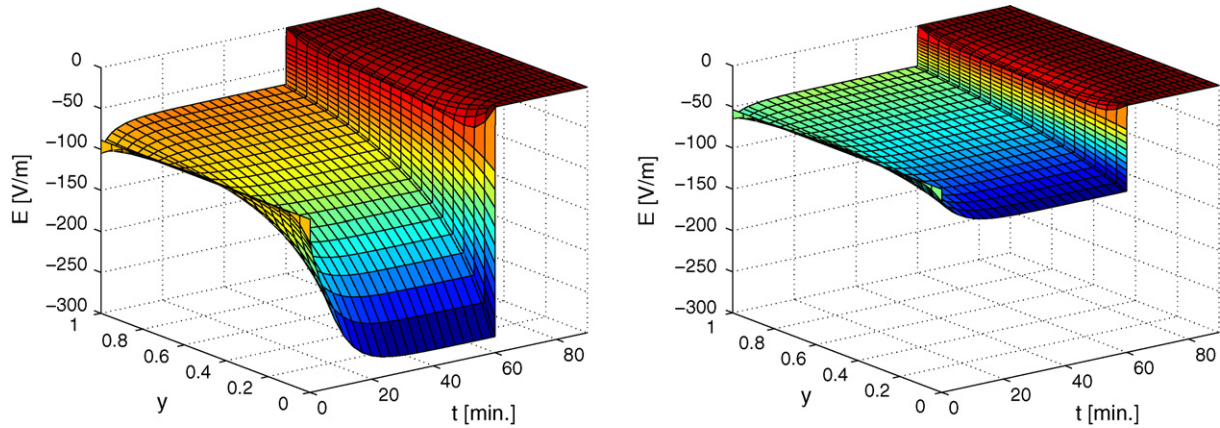


Fig. 7. Development of the $E(y,t)$ under the same battery operation conditions used in Fig. 5. Left figure represents case without support salt, right one is with support salt added.

which implies that

$$c_{PF_6^-}(y) = \frac{c_{PF_6^-}^0}{c_0} \frac{I}{2FAD_{Li^+}} \left(y - \frac{L}{2} \right) + c_{PF_6^-}^0 \quad (43)$$

Similar derivations for $c_{ClO_4^-}$ result in

$$c_{ClO_4^-}(y) = \frac{c_{ClO_4^-}^0}{c_0} \frac{I}{2FAD_{Li^+}} \left(y - \frac{L}{2} \right) + c_{ClO_4^-}^0 \quad (44)$$

The steady-state concentration profiles of the anions are shown in Fig. 3. In contrast to the cation profiles, all anion profiles in the electrolyte are linear and the contribution of each individual species is proportional to the initial salt concentration in the electrolyte.

From Eq. (39) it follows that the electric field $E(y,t)$ is inversely proportional to the total ionic concentration $c(y,t)$. The simulation results are shown in Fig. 4 and reveal that the electric field can be significantly be reduced by more than a factor of 3 in the present

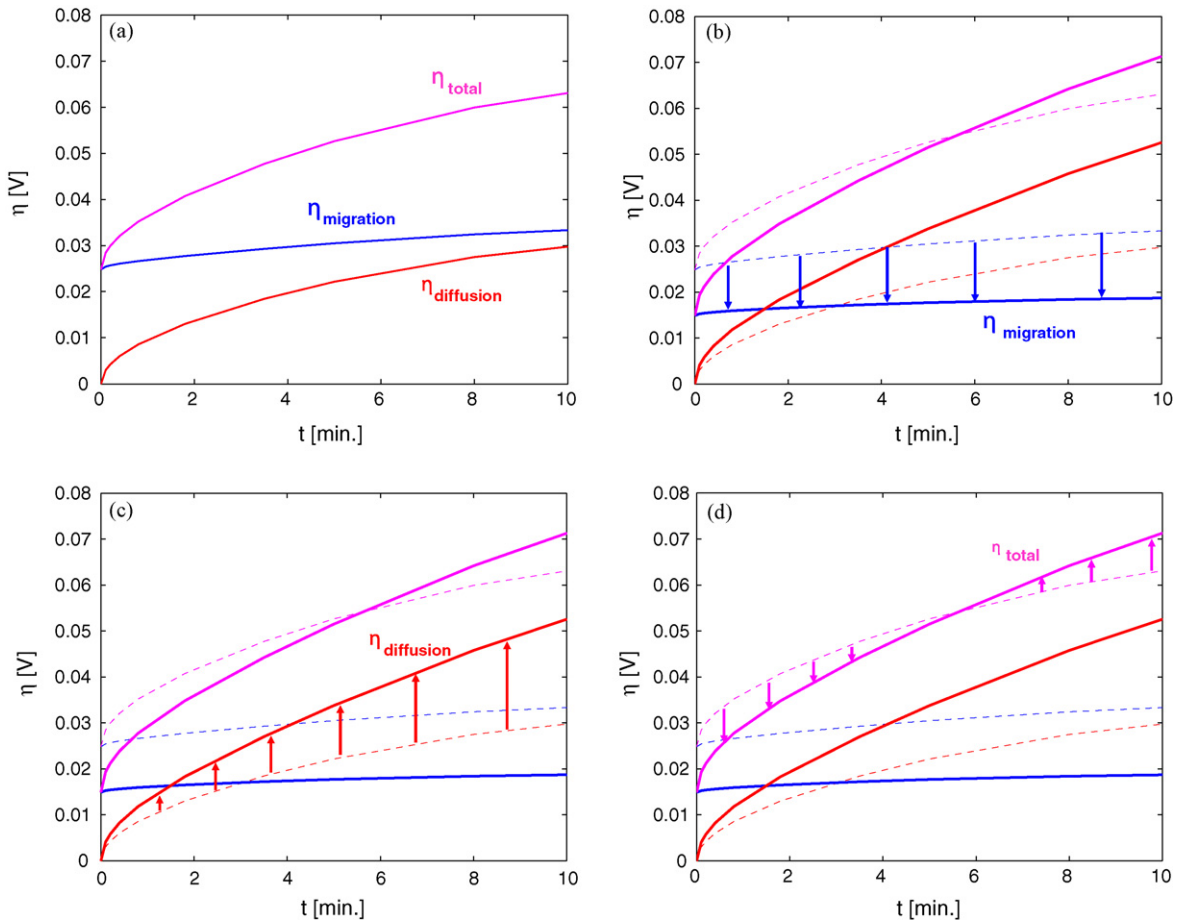


Fig. 8. Overpotentials development with highlighted effects of support salt addition: (a) Case without support salt, (b) effect of salt on migration component, (c) on diffusion component and (d) on total overpotential.

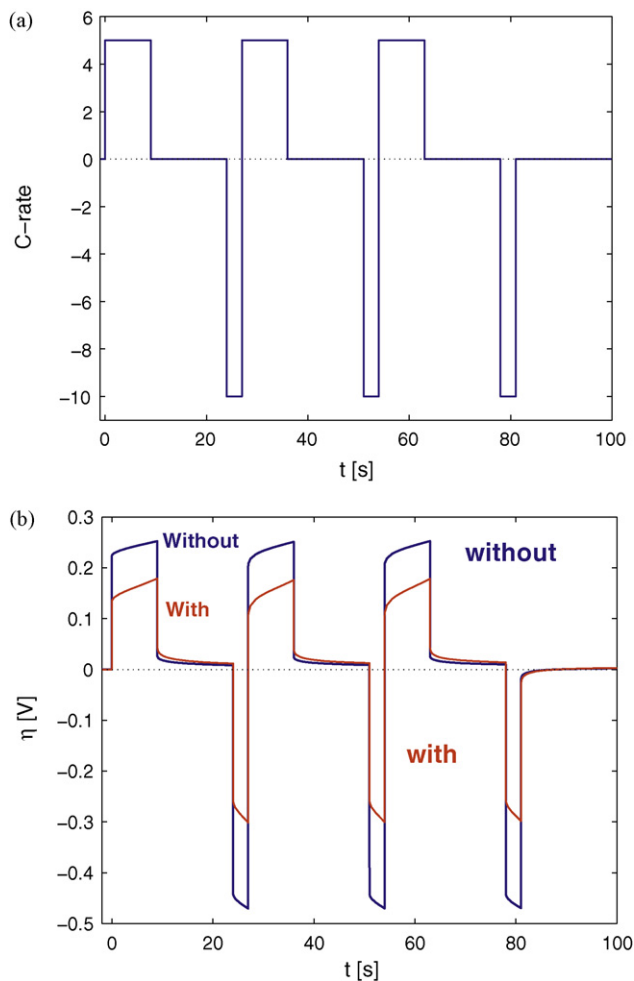


Fig. 9. Pulse (dis)charging a Li-ion battery with the indicated current levels (a) and the resulting calculated development of the total overpotential (b) with (red line) and without (blue line) supportive salt (1 M KClO_4) added to a conventional Li-ion battery electrolyte (1.5 M LiPF_6). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

simulations. This decrease in the electric field is larger where $E(y,t)$ is most pronounced, *i.e.* at $y=0$.

The next four figures illustrate the development of the most relevant concentrations and overpotentials by solving Eqs. (4.1)–(7.4) using $L = 2.8 \times 10^{-4}$ m, $A = 2 \times 10^{-2}$ m², $D_{\text{Li}^+} = D_{\text{K}^+} = 2 \times 10^{-11}$ and $D_{\text{PF}_6^-} = D_{\text{ClO}_4^-} = 3 \times 10^{-11}$ m² s⁻¹ during one hour charging with 0.5 A. Figs. 5 and 6 show the development of $c_{\text{Li}^+}(y, t)$ and $c_{\text{K}^+}(y, t)$ as a function of location and time. At the very first moment of time the concentration profile is completely flat. After turning on the current, a sizable concentration profile develops, to reach the steady-state after approximately 30 min. Both concentration profiles are slightly non-linear in the steady-state. After 60 min the current is switched off and the concentration profiles equilibrate during the subsequent relaxation period. Note that for clarity reasons the y - and t -axes are rotated in Figs. 5 and 6.

Fig. 7 shows the development of the electric field for the case without (a) and with (b) supporting salt in the electrolyte. It can clearly be seen that adding a supportive salt has a very beneficial

effect on the electric field, which is not only reduced in the steady-state (compare with Fig. 4) but also under all transient conditions, including $t=0$.

The above results show that adding supportive salts is an efficient way to reduce the electric field across the electrolyte. However, according to Eq. (12), the total overpotential across the electrolyte not only depends on the electric field, but also on the ionic salt concentrations. Fig. 8a shows the development of the diffusion-, migration- and total overpotentials during first 10 min of charging when no supportive salt is present in the electrolyte. When the current is switched on at $t=0$, the contribution of diffusion is zero and all overpotential is determined by migration only. The diffusion component develops, however, more rapidly in time to become almost equally important under steady-state.

Fig. 8b–d illustrates the influence of supportive salt onto the various overpotential components. Fig. 8b shows how migration overpotential is reduced by the addition of supportive salt. Fig. 8c, on the other hand, unravels that the diffusion component grows in time when a supporting salt is added. Both the migration and diffusion effects combine in the total overpotential behavior (Fig. 8d). It can be seen, in this example, that the addition of a neutral salt reduces the total overpotential up to about 6 min charging to become larger after that. These results imply that electrolytes with neutral salt additives will operate more effectively when used in a pulse (dis)charge mode, which is most important in, for example, power tools and automotive applications.

Fig. 9 shows, as an example, the impact of such (dis)charging current pulses (a) has on the development of the total overpotential (b) for the case with (red line) and without (blue line) a supportive salt containing electrolyte. An overpotential reduction across the electrolyte of more than 40% has been achieved in these simulations.

5. Conclusions

A one-dimensional model has been proposed to simulate the ionic conductivity of advanced organic electrolytes in Li-ion batteries, including the case that a supportive salt is added to conventional electrolytes. The model consists of four coupled parabolic-type of partial differential equations. Several cases have been theoretically investigated. It was found that adding a supportive salt is efficient to decrease the electric field across the electrolyte and hence to reduce the migration overpotential. The diffusion overpotential may, however, become more pronounced, resulting from the opposite concentration gradients build up by the “supportive” ions. When batteries are subjected to short (dis)charge pulses, significant overpotentials reductions has been calculated. Consequently, significant energy loss reductions are predicted under these conditions.

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