Some comments on the Butler-Volmer equation for modeling Lithium-ion batteries

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Abstract

In this article the Butler-Volmer equation used in describing Lithium-ion (Li-ion) batteries is discussed. First, a complete mathematical model based on a macro-homogeneous approach developed by Neuman is presented. Two common mistakes found in the literature regarding a sign in a boundary conditions and the use of the transfer coefficient are mentioned. The paper focuses on the form of the Butler-Volmer equation in the model. It is shown how practical problems can be avoided by taking care in the form used, particularly to avoid difficulties when the solid particle in the electrodes approach a fully charged or discharged state or the electrolyte gets depleted. This shows that the open circuit voltage and the exchange current density must depend on the lithium concentration in both the solid and the electrolyte in a particular way at the extremes of the concentration ranges.

Keywords: Lithium-ion batteries, Butler-Volmer equation, mathematical model.

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1 Introduction

Lithium-ion (Li-ion) batteries have become very popular in the last years as efficient energy storage devices. A mathematical model demonstrating the role of the key factors in the battery operation can be very helpful for the design and optimization of new models and also for the real-time control of its performance.

Based on a macro-homogeneous approach developed by Neuman [1], several mathematical models have been developed for these purposes (cf. [2, 3, 4, 5, 6, 7, 8, 9, 10], which include the main physics present in charge/discharge processes. A complete mathematical model is presented in Section 2 including a system of boundary value problems for the conservation of Lithium and conservation of charge in the solid and electrolyte phases. In that section we remark that several authors have included a boundary condition that is not correct (see [11] and Remark 5). Although the authors have probably used the correct boundary condition when solving the model numerically the reader should be aware of the right choice. A second common mistake involving the role of the transfer coefficient in the equation for conservation of charge in the electrolyte is also pointed out (see Remark 2).

Once we have presented the model, Section 3 is devoted to the Butler-Volmer equation. It is shown that care must be taken in the form of this equation especially in the limiting cases where the electrodes approach a fully charged or discharged state or the local electrolyte concentration reduces substantially. In such cases it is necessary to ensure the equation allows particles to discharge or charge but only in direction that ensures concentrations remain in the physically relevant regime.

2 Mathematical model

2.1 Generalities

Let us assume we have a general binary electrolyte (i.e. a single salt composed of one kind of cation and one kind of anion) conducting electricity and there is no convection involved in the process. In order to give a general idea of the equations involved in the model detailed in Section 2.2 below, we use the infinite dilute solution theory (we could also use the concentrated solution theory, see [11], which is more complex and accurate but leads to equations
of the same type).

The accumulation of ions is due to the net flux and the production, i.e.

\[ \frac{\partial c_i}{\partial t} = -\nabla \cdot N_i + R_i \quad (i \in \{+, -\}), \]  

(1)

where \( R_i \) (mole m\(^{-3}\) s\(^{-1}\)) is the reaction rate and \( N_i \) is the flux (mole m\(^{-2}\) s\(^{-1}\)) of anions \((N_-)\) and cations \((N_+)\) in the electrolyte. This flux is due to migration and diffusion and is given by

\[ N_i = -z_i u_i F c_i \phi_e - D_i \nabla c_i \quad (i \in \{+, -\}), \]  

(2)

where \( c_+, c_- \) are the molar concentration (mol m\(^{-3}\)) of cations and anions, \( z_+, z_- \) are the number of protons charges carried by a cation and by an anion, \( u_+, u_- \) are the mobility of cations and anions (m\(^2\) mole J\(^{-1}\) s\(^{-1}\)) and \( D_+, D_- \) are the diffusion coefficient of cations and anions (m\(^2\) s\(^{-1}\)).

We assume the solution is electrically neutral, i.e.

\[ z_+ c_+ + z_- c_- = 0 \]  

(3)

Let \( \nu_+, \nu_- \) be the number of cations and anions produced by the dissociation of one molecule of electrolyte, i.e.

\[ z_+ \nu_+ + z_- \nu_- = 0. \]

and

\[ c_e = \frac{c_+}{\nu_+} = \frac{c_-}{\nu_-} \quad \text{(so called, concentration of the electrolyte)} \]

Assuming \( u_+ \) and \( u_- \) are constant, if we multiply (1) by \( \frac{1}{\nu_\pm} \) we get

\[ \frac{\partial c}{\partial t} - z_+ u_+ F \nabla \cdot (c \nabla \phi_e) - \nabla \cdot (D_+ \nabla c) = \frac{R_+}{\nu_+}, \]

\[ \frac{\partial c}{\partial t} - z_- u_- F \nabla \cdot (c \nabla \phi_e) - \nabla \cdot (D_- \nabla c) = \frac{R_-}{\nu_-}. \]

Subtraction of these two equaitons gives

\[ (z_+ u_+ - z_- u_-) F \nabla \cdot (c \nabla \phi_e) + \nabla \cdot ((D_+ - D_-) \nabla c) = \frac{R_-}{\nu_-} - \frac{R_+}{\nu_+}, \]
which can be used to eliminate $\nabla \phi_e$ from either of the previous equations in order to get the equation for the conservation of ions

$$\frac{\partial c_e}{\partial t} - \nabla \cdot (D_e \nabla c_e) = R,$$

where

$$D_e = \frac{z_+ u_+ D_- - z_- u_- D_+}{z_+ u_+ - z_- u_-}, \quad R = \frac{z_+ u_+ R_- - z_- u_- R_+}{z_+ u_+ - z_- u_-}.$$

The diffusion $D_e$ and reaction $R$ coefficients represent a compromise between the diffusion and the reaction coefficients of the anion and the cation.

Regarding the electrical current in the electrolyte, we have that

$$i_e = F(z_+ N_+ + z_- N_-),$$

where $i_e$ is current density ($\text{A m}^{-2}$). Then, from (1)–(4) it can be deduced that

$$- \nabla \cdot i_e \frac{RT}{z_+ \nu_+ F} = \frac{R_-}{\nu_-} - \frac{R_+}{\nu_+},$$

and, using the Nernst-Einstein equation, $D_i = RT u_i$, that

$$i_e = -\kappa \nabla \phi_e - \frac{RT \kappa}{F} \left( \frac{t_+}{z_+} + \frac{t_-}{z_-} \right) \nabla \ln c_e,$$

where $\kappa = F^2 ((z_+)^2 u_+ c_+ + (z_-)^2 u_- c_-)$ is electrical conductivity of the electrolyte and

$$t_+ = \frac{z_+ u_+}{z_+ u_+ - z_- u_-}, \quad t_- = \frac{-z_- u_-}{z_+ u_+ - z_- u_-} = 1 - t_+$$

are the so-called transference numbers. Hence, from (5) and (6) we obtain the equation for the conservation of charge

$$- \nabla \cdot (\kappa \nabla \phi_e) - \frac{RT}{F} \left( \frac{t_+}{z_+} + \frac{t_-}{z_-} \right) \nabla \cdot (\kappa \nabla \ln c_e) = z_+ \nu_+ F \left( \frac{R_+}{\nu_+} - \frac{R_-}{\nu_-} \right).$$

**Remark 1** For $\text{Li}^+$ batteries with $z_+ = 1$, $z_- = -1$, $\nu_+ = \nu_- = 1$ and $R_- = 0$ (i.e. the cation is the only ion reacting at the electrode) the following equations are satisfied in the electrolyte:

$$\frac{\partial c_e}{\partial t} - \nabla \cdot (D_e \nabla c_e) = \frac{1 - t_+}{F} j_i \text{Li} \quad (\text{conservation of ions})$$
\[-\nabla \cdot (\kappa \nabla \phi_e) - \frac{RT}{F} (2t_+ - 1) \nabla \cdot (\kappa \nabla \ln c_e) = j^{Li} \quad \text{(conservation of charge)}.
\]

We have used that, due to the Faraday’s laws of electrolysis, \( R_+ = \frac{1}{F} j^{Li} \), where \( j^{Li} = \frac{\partial \phi_e}{\partial x} \) is the reaction current (A m\(^{-3}\)) resulting in production or consumption of Li\(^+\).

### 2.2 The complete model

A typical Li-ion battery cell has three regions: A porous negative electrode, a porous positive electrode and an electron-blocking separator. In all these regions there is an electrolyte containing various charge species, including lithium, that can move all through the cell in response to an electrochemical potential gradient.

A 1D electrochemical model is considered for the evolution of the Li concentration \( c_e(x, t) \) (mol m\(^{-3}\)) and the electric potential \( \phi_e(x, t) \) (V) in the electrolyte and the electric potential \( \phi_s(x, t) \) (V) in the solid electrodes, along the \( x \)-direction, with \( x \in (0, L) \) and \( L = L_1 + \delta + L_2 \) being the cell width (m). We assume that \( (0, L_1) \) corresponds to the negative electrode, \( (L_1, L_1 + \delta) \) corresponds to the separator and \( (L_1 + \delta, L) \) corresponds to the positive electrode. The lithium behavior in the electrolyte is coupled with a diffusion model for the evolution of the Li concentration \( c_s(x, r, t) \) in a generic solid spherical electrode particle. Spherical symmetry of this diffusion is assumed along the radial \( r \)-direction in the region \( r \in [0, R_s] \) where \( R_s \) (m) is the average radius of a generic particle. Using a 1D approximation for the entire battery is valid since the characteristic length scale of a typical Li-ion cell along the \( x \)-axis is on the order of 100 µm, whereas the characteristic length scale for the remaining two axes is on the order of 100,000 µm or more (cf. [9]). Note that \( R_s \) can be different in each electrode (\( R_{s, -}, R_{s, +} \)).

Based on the conservation equations deduced in Remark [1] and the models appearing in the literature (cf. [2] [3] [4] [5] [6] [7] [8] [9] [10]), along with the additional assumption of constant diffusion and activity electrolyte coefficients, a model for the performance of a battery at constant temperature, is given by system of equations (8)–(11):
\[
\begin{aligned}
\epsilon_e \frac{\partial c_e}{\partial t} - D_e \frac{\partial}{\partial x} \left( \epsilon_e^n \frac{\partial c_e}{\partial x} \right) &= \frac{1 - t_0^2}{F} j^\text{Li}, \quad \text{in} \ (0, L) \times (0, t_{\text{end}}), \\
\frac{\partial c_e}{\partial x}(0, t) &= \frac{\partial c_e}{\partial x}(L, t) = 0, \quad t \in (0, t_{\text{end}}), \\
c_e(x, 0) &= c_{e, 0}(x), \quad x \in (0, L),
\end{aligned}
\]

For each \( x \in (0, L_1) \cup (L_1 + \delta, L) \):
\[
\begin{aligned}
\frac{\partial c_s}{\partial t} - \frac{D_s}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial c_s}{\partial r} \right) &= 0, \quad \text{in} \ (0, R_s) \times (0, t_{\text{end}}), \\
\frac{\partial c_s}{\partial r}(x; 0, t) &= 0, \quad -D_s \frac{\partial c_s}{\partial r}(x; R_s, t) = \frac{R_s(x)}{3\epsilon_s(x)F} j^\text{Li}, \quad t \in (0, t_{\text{end}}), \\
c_s(x; r, 0) &= c_{s, 0}(x; r),
\end{aligned}
\]

For each \( t \in (0, t_{\text{end}}) \):
\[
\begin{aligned}
-\frac{\partial}{\partial x} \left( \epsilon_e^n \frac{\partial \phi_e}{\partial x} \right) + (1 - 2t_0^2) \frac{RT}{F} \frac{\partial}{\partial x} \left( \epsilon_e^n \frac{\partial \phi_e}{\partial x} \ln (c_e) \right) &= j^\text{Li} \quad \text{in} \ (0, L), \\
\frac{\partial \phi_e}{\partial x}(0, t) &= \frac{\partial \phi_e}{\partial x}(L, t) = 0,
\end{aligned}
\]

For each \( t \in (0, t_{\text{end}}) \):
\[
\begin{aligned}
-\epsilon_s \frac{\partial^2 \phi_s}{\partial x^2} &= -j^\text{Li} \quad \text{in} \ (0, L_1) \cup (L_1 + \delta, L), \\
\epsilon_s(0) \sigma(0) \frac{\partial \phi_s}{\partial x}(0, t) &= \epsilon_s(L) \sigma(L) \frac{\partial \phi_s}{\partial x}(L, t) = -\frac{I(t)}{A}, \\
\frac{\partial \phi_s}{\partial x}(L_1, t) &= \frac{\partial \phi_s}{\partial x}(L_1 + \delta, t) = 0.
\end{aligned}
\]

In this system of equations the independent variable are position \( x \) (m) and time \( t \) (s) with dependent variables \( c_e = c_e(x, t) \) (mol m\(^{-3}\)), \( c_s = c_s(x; r, t) \) (mol m\(^{-3}\)), \( \phi_e = \phi_e(x, t) \) (V), \( \phi_s = \phi_s(x, t) \) (V), and \( I = I(t) \) (A) the applied current. Parameters in the model are \( p \) the Bruggeman porosity exponent (nondimensional constant), \( D_e \) the electrolyte diffusion coefficient (m\(^2\) s\(^{-1}\)),
$t_0^+$, the transference number of Li$^+$, $\kappa = \kappa(\epsilon_e(x, t))$ the electrolyte phase ionic conductivity (S m$^{-1}$), and $A$ (m$^2$) is the cross-sectional area (also the current collector area). There are parameters that take different values in different regions and these are $\epsilon_e$ ($\epsilon_{e,-}$ if $x \in (0, L_1)$, $\epsilon_{e,sep}$ if $x \in (L_1, L_1 + \delta)$ and $\epsilon_{e,+}$ if $x \in (L_1 + \delta, L)$) which is the volume fraction of the electrolyte, $D_s$ ($D_{s,-}$ if $x \in (0, L_1)$, $D_{s,+}$ if $x \in (L_1 + \delta, L)$) which is the solid phase Li diffusion coefficient (m$^2$ s$^{-1}$), $\epsilon_s$ ($\epsilon_{s,-}$ if $x \in (0, L_1)$, $\epsilon_{s,+}$ if $x \in (L_1 + \delta, L)$) which is the volume fraction of the active materials in the electrodes, $\sigma_s$ ($\sigma_{s,-}$ if $x \in (0, L_1)$, $\sigma_{s,+}$ if $x \in (L_1 + \delta, L)$) which is the electrical conductivity of solid active materials in an electrode (S m$^{-1}$), and $j_{Li}$ (A m$^{-2}$) is the reaction current resulting from intercallation of Li into solid electrode particles.

For $j_{Li}$ the following Butler-Volmer equation is commonly used (cf. [2, 4, 6, 7, 8, 9, 10])

\[
\begin{align*}
    j_{Li} &= \begin{cases} 
    \frac{3\epsilon_s(x)}{R_s(x)}i_0 \left[ \exp \left( \frac{\alpha_a F}{R T} \eta \right) - \exp \left( -\frac{\alpha_c F}{R T} \eta \right) \right] & \text{if } x \in (0, L_1) \cup (L_1 + \delta, L), \\
    0 & \text{if } x \in (L_1, L_1 + \delta) 
    \end{cases}
\]
(12)

(here, for the sake of simplicity, we have considered the solid/electrolyte interfacial film resistance to be zero and therefore is not included in the above equation), where $T$ (K) is the temperature of the cell, $a_s(x) = \frac{3\epsilon_s(x)}{R_s(x)}$ (m$^{-1}$) is the specific interfacial area of electrodes, $i_0 = i_0(x, \epsilon_s, \epsilon_e)$ (A m$^{-2}$) is the exchange current density of an electrode reaction, $\alpha_a, \alpha_c$ (dimensionless) are anodic and cathodic transfer coefficients for an electrode reaction, and $\eta$ (V) is the surface overpotential (V) of an electrode reaction.

Most of the parameters in the Butler-Volmer equation are agreed upon in models but there is considerable variation in the behavior of $i_0$ and $\eta$. Typically

\[
\eta = \begin{cases} 
    \phi_s - \phi_e - U(x, \epsilon_s), & \text{if } x \in (0, L_1) \cup (L_1 + \delta, L), \\
    0 & \text{if } x \in (L_1, L_1 + \delta), 
    \end{cases}
\]

where $U(x, \epsilon_s)$ is the equilibrium potential (V) at the solid/electrolyte interface (i.e. the open circuit voltage, OCV, of each electrode). An empirical function is usually exploited for $U$ taking different forms in the two electrodes
and dependent only on the local surface concentration of lithium with

\[
U = \begin{cases} 
U_-(\frac{c}{c_{s,\text{max}}}) & \text{if } x \in (0, L_1), \\
U_+(\frac{c}{c_{s,\text{max}}}) & \text{if } x \in (L_1 + \delta, L), 
\end{cases}
\]

The functions \(U_-, U_+\) are typically obtained from fitting experimental data and the constants \(c_{s,\text{+,max}}, c_{s,\text{-,max}}\) (mol m\(^{-3}\)) taken as the maximum possible concentration in the solid positive and negative electrode, respectively. The exchange current \(i_0\) is taken in different forms including being constant and being

\[
i_0 = \begin{cases} 
k_- c_o^{\alpha_a} (c_{s,\text{-,max}} - c_s)^{\alpha_a} c_s^{\alpha_c} & \text{if } x \in (0, L_1), \\
k_+ c_o^{\alpha_a} (c_{s,\text{+,max}} - c_s)^{\alpha_a} c_s^{\alpha_c} & \text{if } x \in (L_1 + \delta, L), 
\end{cases}
\]

where \(k_-, k_+\) are kinetic rate constants (A m\(^{-2+6\alpha_a+3\alpha_c}\) mol\(^{-2\alpha_a-\alpha_c}\)). In the final section we concentrate on the appropriateness of the functional form of \(U\) and \(i_0\).

**Remark 2** The second term on the left hand side of system (10) is often written in the literature, using \((1 - t_0^0)\) (see [2], [3]) or \(2(1 - t_0^0)\) (see [4], [6], [7], [8], [9], [10]), instead of \((1 - 2t_0^0)\), which is the term deduced in Remark 1.

**Remark 3** This system of equations does not have uniqueness of solution (if \(\phi_s(x, t)\) and \(\phi_e(x, t)\) are solutions then \(\phi_s(x, t) + c(t)\) and \(\phi_e(x, t) + c(t)\) are also solutions, for any function \(c(t)\)). A way of avoiding that is to set a reference value of \(\phi_s(x, t)\) or \(\phi_e(x, t)\) at some point \(x\). For instance we can impose \(\phi_s(0, t) = 0\) for any \(t \in [0, t_{\text{end}}]\). Some results regarding the existence and uniqueness of solution can be seen in [11].

**Remark 4** After solving the above model, we can estimate the state of the charge of the negative electrode \(SOC_-(t)\) and of the positive one \(SOC_+(t)\), and the cell voltage \(V(t)\), at time \(t\), by computing

\[
SOC_-(t) = \frac{3}{L_1(R_{s,-})^3} \int_0^{L_1} \int_0^{R_{s,-}} \frac{r^2 c_s(x; r, t)}{c_{s,\text{-,max}}} dr dx,
\]

\[
SOC_+(t) = \frac{3}{(L - L_1 - \delta)(R_{s,+})^3} \int_{L_1+\delta}^{L} \int_0^{R_{s,+}} \frac{r^2 c_s(x; r, t)}{c_{s,\text{+,max}}} dr dx,
\]

The functions \(U_-, U_+\) are typically obtained from fitting experimental data and the constants \(c_{s,\text{+,max}}, c_{s,\text{-,max}}\) (mol m\(^{-3}\)) taken as the maximum possible concentration in the solid positive and negative electrode, respectively. The exchange current \(i_0\) is taken in different forms including being constant and being

\[
i_0 = \begin{cases} 
k_- c_o^{\alpha_a} (c_{s,\text{-,max}} - c_s)^{\alpha_a} c_s^{\alpha_c} & \text{if } x \in (0, L_1), \\
k_+ c_o^{\alpha_a} (c_{s,\text{+,max}} - c_s)^{\alpha_a} c_s^{\alpha_c} & \text{if } x \in (L_1 + \delta, L), 
\end{cases}
\]
\[ V(t) = \phi_s(L, t) - \phi_s(0, t) - \frac{R_f}{A} I(t), \]

where there is a constant film resistance of \( R_f \).

**Remark 5** In [4], [6], [7], [8], [10], authors use the following (incorrect) boundary conditions at \( x = 0 \) and \( x = L \), instead of those presented in (11):

\[
- \varepsilon_{s,-} \frac{\partial \phi_s}{\partial x}(0, t) = \varepsilon_{s,+} \frac{\partial \phi_s}{\partial x}(L, t) = \frac{I(t)}{A}. \quad (14)
\]

We note in passing that if this incorrect condition is used then it can be proved (see [11]) that the corresponding system of boundary value problems does not have any solution unless \( I(t) \equiv 0 \).

### 3 The Butler-Volmer equation

The Butler-Volmer equation in the mathematical model presented here has a general functional form widely used in the literature (cf. [2, 3, 4, 6, 7, 8, 9, 10]), but it is necessary to take care in the detailed functions used for \( U \) and \( \eta \) as explained below. We note that both \( i_0 \) and \( U \) may vary with \( c_s \) and \( c_e \) throughout the relevant range of these concentrations but we are only interested in ensuring that the behavior is appropriate when the electrodes get close to being fully intercollated \( c_s = c_s, \pm, \text{max} \), are fully depleted \( c_s = 0 \), or where the electrolyte is completely depleted \( c_e = 0 \). To discuss the possible behavior we consider the case \( c_s \rightarrow 0 \) and then indicate how this can be extended to the other cases.

Consider therefore the case \( c_s \rightarrow 0 \) while \( U \) tending to a constant and \( i_0 \) is given by (13) so that \( i_0 \rightarrow 0 \). It might be expected that the Li flux out of the particle will therefore cease as \( c_s \rightarrow 0 \) thereby preventing negative concentrations in the solid. However, this condition also implies that if we start with a depleted particle then no flux can ever enter the particle. Such a physically unrealistic situation should not be allowed in the model.

Alternative formulations of \( i_0 \) and \( U \) can avoid this problem in various ways and it is always possible to simply chose these functions and then impose some switching logic to turn the flux on or off as required to avoid such problems. However, it may be preferable to have the Butler-Volmer condition designed, through the modeling of suitable physical mechanisms, to ensure such physically irrelevant situations cannot occur.
Hence we would like to have the property that, as \( c_s \to 0 \) the flux can only take negative values. Such a property can readily be achieved by ensuring that \( U \to \infty \) as \( c_s \to 0 \) as this will ensure that the negative exponential dominates the Butler-Volmer condition. A common physical condition is to consider that, as \( c_s \to 0 \) the forward (cathodic) should be of zeroth order in \( c_s \) while the reverse (anodic) reaction should be first order. Such behavior can be readily achieved by taking \( i_0 \) and \( U \) to have the local form, when \( c_s \to 0 \),

\[
i_0 \approx (k c_s)^{\alpha_a/\alpha_a + \alpha_c} \quad \text{and} \quad U \approx \frac{-RT}{F(\alpha_a + \alpha_c)} \ln (k c_s),
\]

where \( k \) is a positive constant (which can be different for each electrode and also can change inside non-homogeneous electrodes). Such a formulation near this extreme of the concentration will automatically ensure the flux cannot become positive at this limit of the concentration reduces, thereby avoiding negative concentrations, and the flux can be finite and positive in this limit so the particle can be charged from a completely depleted state. Note that a reverse reaction of order greater than one can be analyzed but this is not usually considered.

Such local behavior of the Butler-Volmer condition is included in some formulation but these need to include all possibilities including extremely low electrolyte concentrations.

Therefore, a reasonable Butler-Volmer formulation would be one where

\[
i_0(x, c_s, c_e) = i_a(x, c_s)^{\alpha_a/\alpha_a + \alpha_c} i_c(x, c_e, c_s)^{\alpha_c/\alpha_a + \alpha_c} \quad (15)
\]

and

\[
U(x, c_s, c_e) = \frac{RT}{F(\alpha_a + \alpha_c)} \ln \left( \frac{i_c(x, c_e, c_s)}{i_a(x, c_s)} \right). \quad (16)
\]

The functions \( i_a \) and \( i_c \) must be strictly positive except at the extremes of the concentrations and locally these functions must take the form:

i) as \( c_s \to 0 \)

\[
i_a(x, c_s) \approx k_a(x) c_s,
\]

with \( k_a(x) = k_{a,+} \) or \( k_{a,-} \), if \( x \in (0, L_1) \) or \( x \in (L_1 + \delta, L) \), respectively (again, non-homogeneous electrodes could also be considered).

ii) as \( c_s \to c_{s,\pm,\text{max}} \)

\[
i_c(x, c_e, c_s) \approx k_{c,s}(x, c_e) (c_{s,\pm,\text{max}} - c_s).
\]
and

\[ \text{iii) as } c_e \to 0 \]

\[ i_c(x, c_e, c_s) \approx k_{c,e}(x, c_s) c_e. \]

Note there may also be a need to consider a maximum electrolyte concentration to avoid precipitation and this might be accommodated in a similar manner.

Notice four important features of the approach proposed here in contrast with what is commonly found in the literature:

1. The function \( U \), the OCV, also depends on \( c_e \) (instead of being independent of it).

2. If \( c_s \to 0 \), then \( i_0 \to 0 \) and \( U \to \infty \) (instead of tending to a finite value) so that

\[ j_{\text{Li}} \approx \frac{3 \varepsilon_s}{R_s} \left( B_1 c_s \exp \left( \frac{\alpha_s F}{R T} (\phi_s - \phi_e) \right) - D_1 \exp \left( -\frac{\alpha_s F}{R T} (\phi_s - \phi_e) \right) \right) \]

for some strictly positive constants \( B_1 \) an \( D_1 \).

3. If \( c_e \to 0 \), then \( i_0 \to 0 \) and \( U \to -\infty \) so that

\[ j_{\text{Li}} \approx \frac{3 \varepsilon_s}{R_s} \left( B_2 \exp \left( \frac{\alpha_s F}{R T} (\phi_s - \phi_e) \right) - D_2 c_e \exp \left( -\frac{\alpha_s F}{R T} (\phi_s - \phi_e) \right) \right) \]

for some strictly positive constants \( B_2 \) an \( D_2 \).

4. If \( c_s \to c_s,\pm,\text{max} \), then \( i_0 \to 0 \) and \( U \to -\infty \) and

\[ j_{\text{Li}} \approx \frac{3 \varepsilon_s}{R_s} \left( B_3 \exp \left( \frac{\alpha_s F}{R T} (\phi_s - \phi_e) \right) - D_3 (c_s - c_s,\pm,\text{max}) \exp \left( -\frac{\alpha_s F}{R T} (\phi_s - \phi_e) \right) \right) \]

for some strictly positive constants \( B_3 \) an \( D_3 \).

These conditions ensure that the lithium flux is constrained to prevent concentrations in the solid being taken into an unphysical regime and also ensuring that, if the solid is near such extreme conditions, the flux can move the system away from these. This ensures the battery can readily charge from a completely depleted state or discharge from a fully charged state.
Remark 6  The most simple case of functions $i_0$ and $U$ satisfying the above conditions (of course, many other possibilities can be also considered) is obtained with

$$i_a(x, c_s) = \begin{cases} k_{a,-}c_s & \text{if } x \in (0, L_1), \\ k_{a,+}c_s & \text{if } x \in (L_1 + \delta, L), \end{cases}$$

$$i_c(x, c_s, c_e) = \begin{cases} k_{c,-}c_e(c_{s,-}\text{max} - c_s) & \text{if } x \in (0, L_1), \\ k_{c,+}c_e(c_{s,+}\text{max} - c_s) & \text{if } x \in (L_1 + \delta, L). \end{cases}$$

Therefore, according to (16),

$$U(x, c_s, c_e) = \begin{cases} \frac{RT}{F(\alpha_a+\alpha_c)} \ln \left( \frac{k_{c,-}c_e(c_{s,-}\text{max} - c_s)}{k_{a,-}c_s} \right) & \text{if } x \in (0, L_1), \\ \frac{RT}{F(\alpha_a+\alpha_c)} \ln \left( \frac{k_{c,+}c_e(c_{s,+}\text{max} - c_s)}{k_{a,+}c_s} \right) & \text{if } x \in (L_1 + \delta, L). \end{cases}$$

Furthermore, according to (13),

$$i_0(x, c_s, c_e) = \begin{cases} k_{c,-}c_e^{\alpha_a+\alpha_c} \left( c_{s,-}\text{max} - c_s \right)^{\alpha_a+\alpha_c} \left( c_s \right)^{\alpha_a+\alpha_c} & \text{if } x \in (0, L_1), \\ k_{c,+}c_e^{\alpha_a+\alpha_c} \left( c_{s,+}\text{max} - c_s \right)^{\alpha_a+\alpha_c} \left( c_s \right)^{\alpha_a+\alpha_c} & \text{if } x \in (L_1 + \delta, L), \end{cases}$$

with $k_-=k_{a,-}^{\alpha_a}k_{c,-}^{\alpha_c}$ and $k_+=k_{a,+}^{\alpha_a}k_{c,+}^{\alpha_c}$, which coincides with (13) when $\alpha_a + \alpha_c = 1$.

Remark 7  Some authors (cf. [6, 7, 8, 10]) take a constant value for $i_0$ and some of them (cf. [6]) claim that it exhibits modest dependency on electrolyte and solid surface concentration. Although this can be valid for appropriate particular cases, in a general situation this does not seem to be valid, since $i_0$ may vary importantly, with extreme cases when the battery is either fully charged or fully discharged.

4 Conclusions

The Butler-Volmer equation is commonly used in the literature in order to take into account the electrochemical reactions that take place in battery electrodes. It is widely used in mathematical models for the simulation of a Lithium-ion battery, based on a macro-homogeneous approach developed by Neuman [1]. It has been shown that the way this equation is commonly used in these models may create situations where the system becomes nonphysical. Conditions on the functional form of the Butler-Volmer equation that ensure
this will not occur have been presented. Furthermore, some common mistakes that can be found in the literature regarding the mathematical equations of the Neuman-type models have also been pointed out.

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