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Finite element simulations of 3D ionic transportation properties in Li-ion electrolytes

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ABSTRACT

In current work, the ionic transport limitations in the Li-ion battery liquid electrolyte with separator are studied by a finite element method. This theoretical approach is based on the Nernst–Planck equation. It is shown that instead of solving coupled PDE system for concentration and potential, it is sufficient to calculate only the concentration profile in a three-dimensional (3D) structure to obtain a full description of the diffusion–migration ionic transport in the electrolyte in the steady-state. Subsequently, the overpotential and electric field can be calculated by using the provided equations. It was found that diffusion and migration overpotentials are equal in the steady-state. Consequently, two algorithms exploiting electrolyte simulations are proposed and successfully used to calculate the limiting current for the simulated battery system. In the present study a single perforated layer of the separator is inserted into the electrolyte and the simulations are carried out by increasing the complexity of the membrane holes. The ionic transportation dependence on the pore shape was found to be local and limited by the spatial area around the perforated separator.

1. Introduction

Li-ion batteries (LIB) and associated technologies are considered as critical element of the future energy-efficient economy. Improving the performance of LIB is highly important for many fields, including electronics, remote and automotive applications. It is known that the energy losses in Li-ion batteries are substantial due to the limited Li^+ ionic conductivity of the electrolyte [1,2]. Therefore the overall battery performance is negatively influenced by a low ionic conductivity. Furthermore, the ionic conductivity of the electrolyte is strongly influenced by the properties of the separator. Porous separators have a complicated structure, consisting of interconnected system of channels [3]. Direct mathematical modeling of 3D porous structures is computationally demanding, thus traditionally, porous electrode and electrolyte structures are modeled by macroscopic homogeneous mathematical models [4–7]. Material parameters, like effective diffusion coefficients and effective conductivities are calculated, using Bruggeman relations [8]. However, nowadays fast advances in computational technology make it possible to perform direct simulations of the 3D microstructures and to study this kind of complicated structures.

The effects of spherical particle arrangements and size distribution in electrodes on the battery performance have been studied in [9]. The spherical particle approximation was used in [10] to simulate separators. However, such spherical particle approximation for the active material in connection to the electrolyte is often insufficient as the structure of the porous separator is much more complex. Porous separators like Celgard 2400, which consist of long thin channels (see [11]), are obviously not an isotropic material since ions can move through the channel only in one direction. Thus, modeling the ionic transport by using porous medium theories may become inaccurate.

Ionic transport in the electrolyte consists of two components: migration and diffusion. When ionic transport limitations are studied by using alternating current (see e.g. [10,12]) the diffusion part in the transport process is not accounted for. However as shown in [1,13], diffusion limitations dominate the direct current performance of the ionic conductor and must therefore be taken into account.

In the current work, ionic transport through the electrolyte-separator system is studied. The effect of the separator is evaluated by forcing the system to run at limiting currents. When a limiting current is applied to the system, zero concentration values are expected near the surface of one of the electrodes. However, currently available mathematical methods for simulating battery systems under these conditions are difficult to use. If the coupled system of Partial Differential Equations (PDEs) with respect to

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concentrations and electric field is solved numerically and the current specified in boundary conditions exceeds the limiting current, then the concentrations may go out of the physical range, creating numerical singularities and interrupting the calculations. The accuracy of the calculated overpotential may be low due to logarithmic dependence on the Li^+ concentration. However, as shown in [1], it is possible to simulate the ionic transport and calculate the concentration profile, overpotential and electric field in the electrolyte for a homogeneous one-dimensional (1D) system by solving only the diffusion equation for the electrolyte. The electric field and the overpotential are derived from it, making it easy to simulate the electrolyte behavior near the limiting current. However, in [1], the mathematical model is not taking into account the presence of a separator and many other factors, influencing 3D movement of the ions in the electrolyte; the ions are moving directly from one electrode to the other.

In the current work, the theoretical approach proposed in [1] is extended to 3D, systems consisting of a separator and electrolyte; a method is presented for calculating the electric field and overpotential in the binary electrolyte under steady-state (dis)charging conditions of the battery. This approach allows considerable simplifications and may speed up the mathematical modeling of the electrolytes of Li-ion batteries and makes it possible to calculate the limiting (dis)charging currents in the simulations more accurate. The developed method is applied to study the fundamental effects of the model separator to the ionic transport in 1.5 M $LiPF_6$ liquid electrolyte by evaluating the limiting current of the battery and the diffusion coefficients of the electrolyte ions.

2. Theory

2.1. General diffusion–migration problem

Consider the volume filled with electrolyte and denote it as $G \subset R^3$. Denote the boundaries of the electrolyte as $\Gamma = \partial G \subset R^3$ and assume that the (outer) normal vector $\boldsymbol{n}$ of unit length is defined in each point of Γ. Consider a binary electrolyte, for example, $LiPF_6$ and denote the type of ions according to index j where $j = 1$ or $j = 2$ for the positive (Li^+) and negative (e.g. PF_6^-) ions, correspondingly. The concentration of the ions in the electrolyte is denoted as $c_j(\boldsymbol{r},t)$ [mol m^{-3}] and the total flux density [mol m^{-2} s^{-1}] for each type of ion follows the Nernst–Plank equation, according to [14]

$$\boldsymbol{J}_j = \boldsymbol{J}_j(\boldsymbol{r},t) = -D_j \nabla c_j(\boldsymbol{r},t) + \frac{F}{RT} D_j z_j c_j(\boldsymbol{r},t)\boldsymbol{E}(\boldsymbol{r},t) \tag{1}$$

where $\boldsymbol{E}(\boldsymbol{r},t) = -\nabla\varphi(\boldsymbol{r},t)$ is the electric field [V m^{-1}], $\varphi(\boldsymbol{r})$ is the electric potential [V], D_j are the diffusion coefficients [m^2 s^{-1}] and z_j are the valence states ($z_1 = -z_2 = 1$). It is also assumed that the normal component of the flux density of Li^+ ions into G is defined in each point on the boundary, according to $\boldsymbol{n}\cdot\boldsymbol{J}_1(\boldsymbol{r},t)\big|_{\boldsymbol{r}\in\Gamma} = i(\boldsymbol{r},t)/F$, where $i(\boldsymbol{r},t)$ is the current density passing the electrode–electrolyte interface [A m^{-2}]; for negative ions the corresponding boundary condition is blocking, i.e. $\boldsymbol{n}\cdot\boldsymbol{J}_1(\boldsymbol{r},t)\big|_{\boldsymbol{r}\in\Gamma} = 0$. Denote the bulk source terms for each type of ions as $R = R(\boldsymbol{r},t)$ [mol m^{-3} s^{-1}]. The initial concentrations for each type of ions will be denoted as c_j^0. In these notations the general diffusion–migration problem can be written for $j = 1, 2$ as

$$\frac{\partial c_j}{\partial t} = -\nabla\cdot\boldsymbol{J}_j + R \quad \text{in} \quad G, \tag{2.1}$$

$$\boldsymbol{n}\cdot\boldsymbol{J}_1(\boldsymbol{r},t)\big|_{\boldsymbol{r}\in\Gamma} = \frac{i(\boldsymbol{r},t)}{F} \tag{2.2}$$

$$\boldsymbol{n}\cdot\boldsymbol{J}_1(\boldsymbol{r},t)\big|_{\boldsymbol{r}\in\Gamma} = 0 \tag{2.3}$$

$$c_j(\boldsymbol{r},0) = c_j^0. \tag{2.4}$$

In the detached form one can write:

$$\frac{\partial c_1}{\partial t} = \nabla\cdot\left(D_1\nabla c_1 - \frac{F}{RT}D_1 c_1\boldsymbol{E}\right) + R, \tag{3.1}$$

$$\boldsymbol{n}\cdot\left(D_1\nabla c_1 - \frac{F}{RT}D_1 c_1\boldsymbol{E}\right)\Big|_{\boldsymbol{r}\in\Gamma} = \frac{i(\boldsymbol{r},t)}{F} \tag{3.2}$$

$$c_1(\boldsymbol{r},0) = c_1^0 \tag{3.3}$$

and

$$\frac{\partial c_2}{\partial t} = \nabla\cdot\left(D_2\nabla c_2 + \frac{F}{RT}D_2 c_2\boldsymbol{E}\right) + R, \tag{4.1}$$

$$\boldsymbol{n}\cdot\left(D_2\nabla c_2 + \frac{F}{RT}D_2 c_2\boldsymbol{E}\right)\Big|_{\boldsymbol{r}\in\Gamma} = 0 \tag{4.2}$$

$$c_2(\boldsymbol{r},0) = c_2^0 \tag{4.3}$$

Assuming local electroneutrality $c(\boldsymbol{r},t) = c_1(\boldsymbol{r},t) = c_2(\boldsymbol{r},t)$, adding the Eqs. (3.1) and (4.1) multiplied by D_2 and D_1 accordingly and doing the same with Eqs. (3.2) and (4.2) results in

$$\frac{\partial c}{\partial t} = D\,\Delta c + R \tag{5.1}$$

$$\boldsymbol{n}\cdot\nabla c\big|_{\boldsymbol{r}\in\Gamma} = \frac{i(\boldsymbol{r},t)}{2FD_1} \tag{5.2}$$

$$c(\boldsymbol{r},0) = c_0 \tag{5.3}$$

where $D = 2D_1D_2/(D_1 + D_2)$ and $c_0 = c_1^0 = c_2^0$ is initial concentration of ions of each type. Assuming local electroneutrality, subtracting Eqs. (3.1) and (4.1) and multiplying the result with Faraday constant (F) yields to

$$(D_2 - D_1)F\nabla^2 c + \nabla\cdot\left[\frac{F^2 c}{RT}(D_1 + D_2)\boldsymbol{E}\right] = 0 \tag{6.1}$$

Repeating the procedure on the corresponding boundary conditions Eqs. (3.2) and (4.2) leads to

$$\boldsymbol{n}\cdot\left[(D_2 - D_1)F\nabla c + \frac{F^2 c}{RT}(D_1 + D_2)\boldsymbol{E}\right]\Bigg|_{\boldsymbol{r}\in\Gamma} = i(\boldsymbol{r},t) \tag{6.2}$$

Eqs. (6.1) and (6.2) can be simplified by introducing the relation for ionic conductivity $\sigma_{\text{ion}} = (F^2c/RT)(D_2 + D_1)$ and defining $\boldsymbol{j}_{1,2} = (D_2 - D_1)F\nabla c$. Eq. (6) can then be rewritten in a form well suitable for numerical implementation

$$-\nabla\cdot(\sigma_{\text{ion}}\nabla\varphi - \boldsymbol{j}_{1,2}) = 0, \tag{7.1}$$

$$-\boldsymbol{n}\cdot(\sigma_{\text{ion}}\nabla\varphi - \boldsymbol{j}_{1,2})\big|_{\boldsymbol{r}\in\Gamma} = i(\boldsymbol{r},t). \tag{7.2}$$

From Eqs. (7.1) and (7.2) it can be concluded, that the electric potential in the electrolyte can be written in Comsol Multiphysics [15] in the standard form for conductive media problems, with concentration-dependent ionic conductivity and external current density terms leading to simple calculations of the potential in the electrolyte during the time-dependent simulations. One can see, that Eqs. (7.1) and (7.2) are dependent on the concentration but Eqs. (5.1)–(5.3) are not dependent on the electric potential in the electrolyte. Thus, it is possible to calculate the evolution of the concentration profile independently from the potential and current distribution in the electrolyte. Therefore the electric potential in the electrolyte can be calculated separately by solving Eqs. (7.1) and (7.2) or by using segregated solvers. This approach leads to a higher accuracy of the calculations, reducing memory limitations and saving computational time. However, in the steady-state it is possible to simplify the electric field calculations even more.Consider the steady-state in electrolyte without bulk source i.e.

$$R = 0, \quad i(\boldsymbol{r},t) = i(\boldsymbol{r}), \quad \text{and} \quad c(\boldsymbol{r}) = \text{const}, \tag{8}$$