

Geometry-Resolved Electro-Chemistry Model of Li-Ion Batteries

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ABSTRACT

The paper presents a simulation approach to Li-Ion batteries based on geometrically resolved electrodes. This means that solid particles and the space occupied by electrolyte are not overlapping but are represented by contiguous, arbitrarily shaped volumes. The solid-electrolyte interface is explicitly resolved and thus allows detailed modeling of electro-chemical processes that are essential for studying performance of the battery cell. Finite volume method is used to solve the equations governing the mass and thermal energy conservation in solid and electrolyte, as well as the distribution of electric potential. The solution domain is discretized in contiguous control volumes of arbitrary polyhedral shape, with conformal interface between solid and fluid regions. Butler-Volmer equation is used to describe the kinetics of solid-electrolyte interface. For the time being, representative geometries of electrodes are manufactured using CAD-tools, but real geometries obtained using scanning methods will be used in future. One example application is presented and the results are compared to those obtained using a widely accepted one-dimensional method.

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INTRODUCTION

Most models of Li-Ion batteries follow the one-dimensional analysis approach pioneered by Newman [1] and subsequently used by many research groups [2,3,4,5,6,7,8,9]. The major drawback of this approach lies in the fact that the porosity and so liquid-phase salt transport and solid-phase electronic conductivity are not explicitly resolved and the diffusion of Li into and out of solid is modeled using representative spherical particles assuming perfect symmetry. These modeling assumptions limit the achievable accuracy; refinement of spatial computational grid and time steps cannot overcome the modeling error introduced by the above assumptions. The structure of a typical Li-Ion battery cell is shown in Fig. 1, with main dimensions listed in Table 1 (after [3]).

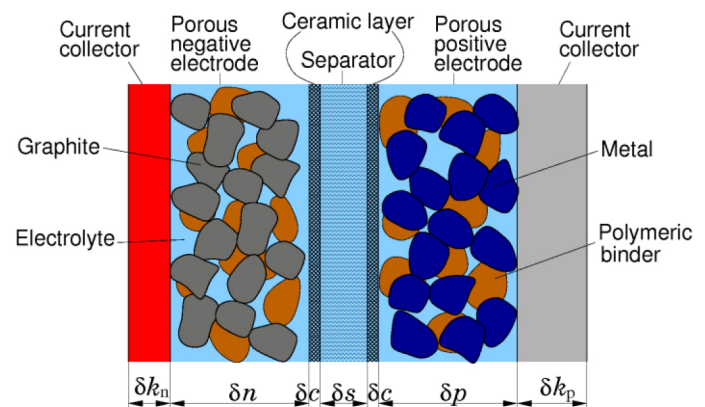


Figure 1. Schematic representation of a section across a Li-Ion battery cell; typical dimensions indicated in the figure are listed in Table 1.

Table 1. Typical dimensions of Li-Ion battery cells (see Fig. 1 for notation).

Thickness of negative current collector	10-20 μm
Thickness of the negative electrode	40-100 μm
Thickness of the separator	15-30 μm
Thickness of the positive electrode	40-100 μm
Thickness of the positive current collector	20-40 μm
Thickness of ceramic layer (if present)	$\sim 5 \mu\text{m}$
Size of active particles in negative electrode	0.1-20 μm
Size of active particles in positive electrode	0.1-20 μm
Size of conducting aid particles	0.01-20 μm

Our intention was to avoid the limitations of the standard approach by resolving the structure of the electrode and explicitly modeling the transport of lithium in the electrolyte and solid phases. The present approach is motivated by the following facts:

- It is nowadays possible to obtain exact geometry of solid particles in electrodes. While the resolution of scanning devices is presently relatively poor for such microscopic structures, there is no doubt that within a few years an adequate resolution will be possible, thus allowing building of CAD-models of solid and fluid regions of battery cell electrodes.
- Commercial software allows creation of quality grids in arbitrarily complex geometries. Grid generation methods based on tetrahedral elements have been available for a long time. These elements are not best suited for diffusion-dominated problems like those in battery electrodes, requiring layered (prismatic) meshes along solid-liquid interfaces. However, over the last decade methods of generating polyhedral grid with prismatic layers along interfaces have been developed [10], allowing for an adequate resolution of complex geometry present in electrodes.
- The computing power is steadily growing and while some industries (like Formula 1 racing car manufacturers) already use computational grids made of hundreds of millions of control volumes, this will become a commonplace in the near future.

Therefore, we decided to develop an approach which will allow a detailed modeling of porous electrodes and associated processes by explicitly separating solid and fluid regions within electrodes and performing a three-dimensional discretization based on finite volume method. For the time being we use manufactured geometries that have similar porosity, tortuosity and active surface area to volume ratio comparable to real electrode material in order to develop the basic models and computational procedure. Real geometries can then be introduced as they become available without the need to modify the solution method. Other research groups are pursuing similar approaches [7].

The next section describes the mathematical model, i.e. the governing equations, constitutive relations and boundary

conditions. Some of the model parameters are based on semi-empirical relations but these can be in the future adapted or replaced by better models as and when they become available. The following section describes briefly the numerical solution method; more details are available in cited references, since the method is widely used in computational fluid dynamics (CFD). Next, an example application of the method to simulate charging and discharging of a unit cell is presented. Results obtained in this simulation are compared to those obtained with a state-of-the-art one-dimensional method. Finally, an outlook of future extensions of the simulation approach is given, with recommendations for further collaboration with research groups conducting experimental studies with Li-Ion batteries, in particular with respect to obtaining an accurate geometry representation of electrode structure and modeling of SEI-processes.

MATHEMATICAL MODEL

The mathematical model of a Li-Ion battery cell consists of the following governing equations:

- Species conservation equations for electrolyte (at least one equation needs to be solved, e.g. for the concentration of Li-salt in a solvent, but depending on the type of electrolyte and chemical reactions involved, multiple species may have to be considered);
- Concentration of Li in active solid material (diffusion into or out of solid material through the SEI);
- Distribution of electric potential in electrolyte;
- Distribution of electric potential in solid part of the electrode (active material and possibly conducting aid);
- Conservation of thermal energy within the whole battery (both solid and liquid part).

The equation describing diffusion of Li into or out of solid active material in electrodes reads (integral form of equations is used because it serves as the starting point for the finite volume method; differential form of all equations is given in [2,3]):

$$\frac{\partial}{\partial t} \int_V c_1 dV = \int_S D_s \nabla c_1 \cdot \mathbf{n} dS \quad (1)$$

It is assumed that diffusion is the only transfer process. Here c_1 is concentration of Li in active solid material, D_s is the corresponding diffusion coefficient, t is time, V is volume, S is control volume surface and $\mathbf{n}$ is the unit vector normal to S .

We assume here a binary electrolyte and express the conservation equation for Li-salt in the liquid phase as follows [2,3]:

$$\frac{\partial}{\partial t} \int_V c_2 dV = \int_S D \nabla c_2 \cdot \mathbf{n} dS \quad (2)$$

where c_2 is the salt concentration in electrolyte, and D is the effective diffusion coefficient, which is defined as [2]:

$$D = D_0 \left(1 - \frac{d \ln c_0}{d \ln c_2} \right) \quad (3)$$

where D_0 is the reference diffusion coefficient and c_0 is the solvent concentration in the liquid phase. Diffusion coefficients in both solid and liquid are assumed to be variable (functions of temperature, concentration etc.). Unless separator is also fully resolved (i.e. liquid region and solid structure geometrically modeled as within electrodes), it is treated as a porous medium; the effects of porosity are then accounted for in the usual way with the help of tortuosity of the electrolyte channels in the separator, τ and the volumetric porosity coefficient, ε [2,3].

Convection by flow of electrolyte has been neglected in Eq. (2); however, it can be added to account for motion caused by expansion or contraction of solid parts of electrodes or by concentration gradients. Since the model is implemented in a general-purpose CFD-code, activating fluid flow is not a problem but this has been left for the next step.

The equation for electric potential in solids follows from Kirchhoff's law:

$$\int_S \sigma \nabla \phi_1 \cdot \mathbf{n} dS = 0 \quad (4)$$

Here σ is the electric conductivity and ϕ_1 the electric potential in the solid phase. The vector of electric current in solid is proportional to the gradient of the potential (Ohm's law): $\mathbf{i}_1 = -\sigma \nabla \phi_1$.

The equation for electric potential in electrolyte is similar to Eq. (4), except for an additional term on the right-hand side resulting from concentration gradient [2]:

$$\int_S \kappa \nabla \phi_2 \cdot \mathbf{n} dS = \int_S \kappa^d \nabla (\ln c_2) \cdot \mathbf{n} dS \quad (5)$$

where κ is the electric conductivity of electrolyte, ϕ_2 is the electric potential in electrolyte and κ^d is the effective conductivity due to concentration gradient, defined as:

$$\kappa^d = \frac{2\kappa RT}{F} \left(1 + \frac{\partial \ln f_A}{\partial \ln c_2} \right) (1 - t_+^0) \quad (6)$$

Here R is the ideal gas constant, T is the temperature, F is the Faraday's constant, t_+^0 is the transference number of Li^+

and f_A is the activity coefficient of Li-salt in electrolyte. The vector of electric current in electrolyte is defined as: $\mathbf{i}_2 = -\kappa \nabla \phi_2 + \kappa^d \nabla (\ln c_2)$.

Finally, the conservation equation for thermal energy leads to the following equation from which temperature is computed:

$$\frac{\partial}{\partial t} \int_V \rho C_p T dV = \int_S \lambda \nabla T \cdot \mathbf{n} dS + \int_V q_h dV \quad (7)$$

Here ρ is the density, C_p is the specific heat at constant pressure, λ is the thermal conductivity and q_h is the total heat source within the control volume, which in general contains contributions from chemical reactions, Joule heating and contact resistance. Since this paper deals with the development of the simulation method, this is left to be a generic variable heat source term which can later be updated.

Equations (1), (2), (4), (5) and (7) are solved for c_1 , c_2 , ϕ_1 , ϕ_2 and T . The appropriate boundary conditions are as follows:

- Neumann boundary conditions apply for c_1 at all boundaries of the solid electrode material. The derivative of concentration in the direction normal to boundary is equal to zero (no mass flux) everywhere except for the SEI, where the gradient is proportional to the current into the SEI from the solid side, j_{1i} (see Fig. 2):

$$\left(\frac{\partial c_1}{\partial n} \right)_{i1} = \frac{j_{1i}}{F D_s} \quad (8)$$

- The same is true for the concentration in electrolyte: the mass flux is zero at all boundaries except for the solid interfaces, where it is proportional to the current out of solid into fluid, j_{2i} :

$$\left(\frac{\partial c_2}{\partial n} \right)_{i2} = \frac{j_{2i}(1 - t_+^0)}{F D} \quad (9)$$

- For the electric potential in solid, Dirichlet boundary condition may apply at the part of current collector through which current flows (specified potential); otherwise, Neumann conditions apply at all other boundaries. The derivative normal to boundary is zero everywhere (no current) except at the solid-electrolyte interfaces, where the following relation between current and potential gradient applies:

$$\left(\frac{\partial \phi_1}{\partial n} \right)_{i1} = -\frac{j_{1i}}{\sigma} \quad (10)$$