



# Electrochemical-mechanical coupled modeling and parameterization of swelling and ionic transport in lithium-ion batteries



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## HIGHLIGHTS

- Implementation of a fully-coupled electrochemical-mechanical model.
- Swelling induced macroscopic mechanical stress due to external compression.
- Parameterization and implementation of pressure-dependent ionic transport.
- Electrical and mechanical validation using a 10 Ah hard case cell.
- Enhanced heterogeneous lithiation of the anode at elevated stress levels.

## ARTICLE INFO

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## ABSTRACT

The intercalation and aging induced volume changes of lithium-ion battery electrodes lead to significant mechanical pressure or volume changes on cell and module level. As the correlation between electrochemical and mechanical performance of lithium ion batteries at nano and macro scale requires a comprehensive and multidisciplinary approach, physical modeling accounting for chemical and mechanical phenomena during operation is very useful for the battery design. Since the introduced fully-coupled physical model requires proper parameterization, this work also focuses on identifying appropriate mathematical representation of compressibility as well as the ionic transport in the porous electrodes and the separator. The ionic transport is characterized by electrochemical impedance spectroscopy (EIS) using symmetric pouch cells comprising  $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$  (NMC) cathode, graphite anode and polyethylene separator. The EIS measurements are carried out at various mechanical loads. The observed decrease of the ionic conductivity reveals a significant transport limitation at high pressures. The experimentally obtained data are applied as input to the electrochemical-mechanical model of a prismatic 10 Ah cell. Our computational approach accounts intercalation induced electrode expansion, stress generation caused by mechanical boundaries, compression of the electrodes and the separator, outer expansion of the cell and finally the influence of the ionic transport within the electrolyte.

## 1. Introduction

Lithium-ion batteries (LIBs), used in the majority of electronic portable devices, such as cell phones and power tools, are the most attractive energy storage in electric vehicles due to their outstanding performance. During the past few years the development of advanced materials, efficient manufacturing technologies and innovative cell designs further increased the energy densities and simultaneously reduced battery production costs. In most of the host materials for state-of-the-art LIBs Li-ion intercalation induces phase transitions upon

charge and discharge. These phenomena lead to intercalation induced volume changes of the active materials finally resulting in swelling of unconstrained cells [1–6] or significant stress formation in cells constrained by rigid casings or module frames [7].

Battery modeling and simulation is a powerful tool for improving LIB design, advance the operating conditions and to get an insight into the internal processes. The first electrochemical-based LIB models were developed by Newman and coworkers [8,9] by applying the concentrated solution and porous electrode theory. Since that time the power of modeling has also been used to understand the mechanical

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contribution to the LIB aging mechanisms. Starting from the microscopic scale, electrochemical-mechanical coupled models were developed to understand stress generation and crack formation within a single active particle during lithiation and delithiation [10–20]. Apart from that there are also models accounting geometry changes in the macroscopic electrode and cell scale existent in literature [5,21–23]. Nevertheless, these models do not involve the dynamic stress generation and the compression of the porous materials, which influences the ionic transport properties.

The focus of this study is the implementation and parameterization of a fully-coupled electrochemical-mechanical model of a Li-ion cell on the macroscopic level. Therefore we firstly introduce in the model a fully-coupled and physically-based description of the electrode expansion effects, stress formation and the ionic transport properties in the porous electrodes or the separator. In our theoretical approach the fundamentals of the electrochemical processes follow Newman's dual foil model [8,9] and the electrode dilation is applied according to our previous work [24]. The current study introduces the physical principles of pore structure compression and its coupling with the electrochemical model. The experimental parameterization focuses on the pressure-dependent electrolyte transport in the electrodes and separator. This can be achieved by determining the ionic resistance of the porous structures in symmetric cells and compressibility measurements. Finally, the implemented model is validated and applied to evaluation of the consequences of elevated pressure conditions.

## 2. Model formulation

In this section the principles of the Li-ion battery simulation model are presented. The introduced mathematical approach for description of porous battery electrodes [8,9] is extended by linking its basics with the mechanical model of porous electrochemically active layers. The fully coupled model is implemented into COMSOL Multiphysics, version 5.2 a.

### 2.1. Electrochemical model

For simplification the active material particles of the electrode are assumed to be of a spherical shape with a mean radius  $R_p$  and homogeneously distributed inside the electrode. This assumption is disputable, since the graphite particles do not have a perfect spherical shape. Nevertheless, referring to other works [25–27] this approximation is also used in this study. The subscripts  $s$  and  $l$  in the equations introduced in this section indicate the solid electrode and liquid electrolyte phase, respectively.

The diffusion driven Li concentration in electrochemically active particles follows Fick's second law presented in spherical coordinates (eq. (1)) using the solid state diffusion coefficient  $D_s$ , particle radius  $r$  and solid phase concentration  $c_s$ .

$$\frac{\partial c_s}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left( D_s r^2 \frac{\partial c_s}{\partial r} \right) \quad (1)$$

The two boundary conditions at the particle surface and the particle center read as

$$\left. \frac{dc_s}{dr} \right|_{r=R_p} = -\frac{i_n}{D_s} \quad \left. \frac{dc_s}{dr} \right|_{r=0} = 0 \quad (2)$$

where  $F$  is the Faraday constant and  $i_n$  the molar current density at the particle surface. The latter can be expressed by Butler-Volmer eq. (3), describing  $i_n$  as a function of applied potential  $\varphi$ .

$$F i_n = i_0 \left[ \exp\left(\frac{\alpha_a F}{RT} \varphi\right) - \exp\left(-\frac{\alpha_c F}{RT} \varphi\right) \right] \quad (3)$$

$R$  corresponds to the universal gas constant,  $T$  to the temperature and  $\alpha_a$  and  $\alpha_c$  to the anodic and cathodic charge transfer coefficient.

The exchange current density  $i_0$  is related to the solid and liquid phase concentrations  $c_s$  and  $c_l$  by the anodic and cathodic reaction rate  $k_a$  and  $k_c$  (eq. (4)).  $c_{s,max}$  represents the maximum Li concentration within the active material and  $c_{l,ref} = 1 \text{ mol. m}^{-3}$ .  $c_{l,ref}$  is merely necessary to achieve consistent units. Since the charge transfer process occurs at the particle surface, the surface concentration of the active material has to be considered in this case.

$$i_0 = F (k_a)^{\alpha_c} (k_c)^{\alpha_a} (c_{s,max} - c_s)^{\alpha_c} (c_s)^{\alpha_a} \left( \frac{c_l}{c_{l,ref}} \right)^{\alpha_c} \quad (4)$$

The electrical current flow  $i_s$  in the solid electrode volume fraction follows Ohm's law, where  $\kappa_s$  is the electronic conductivity and  $\varphi_s$  the solid phase electrical potential (eq. (5)).

$$i_s = -\kappa_s \nabla \varphi_s \quad (5)$$

The mass balance of ions moving in a liquid phase through a porous domain material is expressed by eq. (6) [9] and the boundary condition (eq. (7)) of zero flux at the current collector interface ( $x = 0$ ) and separator interface ( $x = t$ ). In this case,  $t$  corresponds to the coating thickness of the electrode.

$$\phi \frac{\partial c_l}{\partial t} = \nabla (\phi D_l \nabla c_l) + a_s i_n (1 - t_+^0) \quad (6)$$

$$\nabla c_l|_{x=0 \text{ and } x=t} = 0. \quad (7)$$

$\phi$  represents the pore volume fraction of the electrode,  $a_s$  the active surface area and  $t_+^0$  the transference number of Li ions in the liquid solvent.  $t_+^0$  is assumed to be constant in this work, whereas the diffusion coefficient  $D_l$  of the electrolyte depends on the concentration [28].

The potential gradient in the electrolyte calculates as [9]

$$\nabla \varphi_l = -\frac{i_l}{\kappa_l} + \frac{2RT}{zF} (1 - t_+^0) \left( 1 + \frac{\partial \ln f_{\pm}}{\partial \ln c_l} \right) \nabla \ln c_l. \quad (8)$$

where the current density in the liquid phase  $i_l$  follows the principles of charge conservation and is coupled to  $i_s$  and the particle surface flux:

$$\nabla i_l = -\nabla i_s = -F a_s i_n \quad (9)$$

The transport parameters in the liquid phase depend on the porosity and tortuosity. Thereby, the porosity  $\phi$  corresponds to the electrolyte volume fraction in the electrode and the tortuosity  $\tau$  specifies the relative elongation of diffusion path perpendicular through the porous structure. Commonly,  $\sigma_l$  and  $D_l$  are used as effective transport parameters inside the electrodes and separator. The limitation of the equilibrium bulk conductivity  $\kappa_{l,0}$  and bulk diffusivity  $D_{l,0}$  can be expressed by the ionic transport factor  $f$  which includes  $\phi$  and  $\tau$  as follows:

$$\kappa_l = f \kappa_{l,0} \quad (10)$$

$$D_l = f D_{l,0} \quad (11)$$

$$f = \frac{\phi}{\tau} \quad (12)$$

The Bruggeman relation (eq. (13)) connects porosity and tortuosity of porous structures, where the Bruggeman coefficient  $\beta$  becomes 0.5 for an electrode containing ideal spherical particles. Eq. (13) represents the most commonly used formulation.

$$\tau = \phi^{-\beta} \quad (13)$$

While the limitation of ionic transport in battery materials has been proven to be significantly higher than predicted by the Bruggeman approximation ( $\beta = 0.5$ ) [29,30], numerous modeling studies using this value can be found in literature [31–33].

### 2.2. Mechanical model

*Single particle expansion.* Existing theoretical works focusing on the mechanical behavior of Li-ion cells describe the intercalation induced

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