# ADVANCED CONTINUUM LI-ION BATTERY MODELLING FRAMEWORK

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## ABSTRACT

A strong demand on simultaneous increases in energy and power densities, as well as a prolonged lifetime, and increased safety of batteries at low battery costs, calls for virtual prototyping with predictive models in the early development phase. To present significant progress in the area of advanced continuum Li-ion battery models this paper presents: a) an innovative continuum modelling framework that more consistently reproduces real multi-particle size distributions and electrode topology, b) the application of thermodynamically based potential as a function of active particle lithiation in the model of the entire cell, c) consistent integration of performance and degradation models of SEI formation.

The capabilities of the modelling framework were validated on LiFePO<sub>4</sub>. The presented results clearly indicate that the proposed modelling framework features more adequate modelling representation at the level of continuum battery models. This is confirmed by the high relevance of modelled voltage vs. capacity results for low and high discharge rates and the simultaneous high relevance of interparticle transport phenomena, which are in agreement with recent nanoscopic findings. Furthermore, the presented results also confirm that the proposed modelling framework is capable of simulating degradation phenomena and thus enables adequate virtual representation of battery parameters of degraded batteries. These innovative functionalities allow - compared to the current state of the art - for a more efficient and systematic model supported design of battery based energy systems.

**Keywords:** Li-ion battery, continuum modelling, innovative ion wiring, LiFePO<sub>4</sub>, thermodynamically based particle potential, degradation modelling

# NONMENCLATURE

Abbreviations	
DOD EC LFP SEI	depth of discharge ethylene carbonate LiFePO₄ solid electrolyte interphase
Symbols	
A <sub>DC,kl</sub> A <sub>ely,k</sub>	surfaces area being in the direct contacts to neighbouring particles particle surface area exposed to the electrolyte
$a_p$	particle specific surface area
Α <sub>tot,k</sub> α	total surface area of the <i>k</i> -th particle
α α <sub>SEI</sub>	SEI charge transfer coefficient
C <sub>e</sub>	electrolyte concentration
$c_{EC}^0$	bulk electrolyte value of EC concentration
$C_{EC}^{S}$	concentration of EC on the surface of graphite
$c_p$	Li concentration in active particle
$C_{p,max}$	maximal Li concentration in active particle
$\delta_{film}$	SEI thickness
F	Faraday constant
$\Phi_e$	electrolyte phase potential
$\Psi_s$	solid phase potential
n n	SEL overnotential
isel	Butler–Volmer exchange flux
i <sub>ev</sub>	Butler–Volmer Li molar flux across the
<i>J B V</i>	solid/electrolyte interface
j <sub>DC</sub>	direct contact Li molar flux across
	particle/particle interface
j <sub>tot</sub>	total Li molar flux across the particle/electrolyte interface
k	rate constant of reaction
$k_b$	Boltzmann constant
k <sub>SEI</sub>	kinetic rate constant of the SEI formation
M <sub>SEI</sub>	molar mass of the SEI
u u	particle chemical potential

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$\hat{n}_{ij}$	normal unit vector
Р	contact surface permeability
R	ideal gas constant
R <sub>film</sub>	ohmic resistance of the SEI film
$\rho_{SEI}$	specific density of the SEI
Т	temperature
t	time
$U^{ocv}$	open circuit voltage
Ω	regular solution parameter
x	Li stoichiometry in Li <sub>x</sub> FePO <sub>4</sub>

# 1. INTRODUCTION

Batteries are one of the most widespread energy storage devices, covering a very broad range of mobile, and increasingly also stationary applications. They are thus enablers for more sustainable mobility and more user-friendly leisure applications, and with the introduction of renewable energy sources, they are gaining on significance in energy applications.

This broad range of applications aims at common high-level goals. These are: batteries with higher energy and power densities, as well as a prolonged lifetime and increased safety, while simultaneously reducing battery costs. Additionally, this broad range of applications also imposes several application specific objectives, which cover operating temperatures, specific load profiles and specific durability criteria. Therefore, a single design cannot fulfil all requirements in an optimal way and thus tailoring battery design to a specific application, with the aim to approach engineering limits, represents a significant challenge.

One of the more promising approaches to tackle this challenge relies on virtual prototyping with predictive

models in the early development phase, which enables significant reductions in development time and costs. However, such an approach also imposes a significant challenge on the applied modelling framework, which should feature a sufficient level of detail and a sound physical basis, to ensure a sufficiently high prediction capability of the model. This allows for high fidelity exploration of the design space and pinpointing the most promising designs in a virtual environment before the first real prototypes are available.

A promising tools for supporting the early stage design of batteries are continuum battery models, based on or inspired by the pioneering work in the field of continuum battery electrochemical modelling published by Newman et. al in 1975 [1]. Even though Newman theory forms the basis of multiple research [2] and commercial battery models [3], they feature certain deficiencies in the context of present requirements on the advanced battery models. General deficiencies of the continuum models on the level of the negative electrode/separator/positive electrode sandwich can be summarized as:

- they do not adequately represent electrode topology, including ion and electron wiring, *e.g.* the actual size distribution of active material, particle-to-particle connectivity [2, 4];
- they rely on empirical correlations for phenomena that are not modelled, *e.g.* potential as a function of active particle lithiation [4, 5];
- they rely on Fick's diffusion equation, which oversimplifies intra-particle Li transport [2, 3].

This paper presents significant progress in the area of advanced continuum Li-ion battery models with:



Figure 1: Modelling representation from a primary particle to the coupled continuum model. The SEM image of commercial LiFePO<sub>4</sub> cathode material shows agglomeration of primary particles into secondary particles. The size distribution of particles and their connectivity have a profound effect on cell performance modelling and different rates of SEI film formation (e.g. SEI layer).

- an innovative continuum modelling framework that enables more consistent reproduction of real multiparticle size distributions and particle connectivity and, therefore, electrode topology on the level of the entire electrode, by transferring fundamental understanding of materials to the cell level;
- the application of potential as a function of active particle lithiation for a phase separating cathode material that is determined by a thermodynamically consistent derivation,
- a consistent integration of performance and degradation models of SEI formation considering cross interactions of loss of cyclable Li and topological changes of the electrodes on battery performance.

The capabilities of the modelling framework were validated on the LiFePO<sub>4</sub> cathode material, which features non-monotonous particle chemical potential as a function of particle lithiation [6], thus being a representative of a very challenging cathode material for Li-ion battery model validation.

#### 2. MODELLING FRAMEWORK

## 2.1. Electrochemical and transport model

The governing equations for spatially and temporally resolved concentration and potential fields are based on Newman's approach [1] with boundary conditions defined similarly as in [2]. In order to develop an adequate modelling representation of the topology of the cathode, e.g. SEM image in Figure 1, an innovative connectivity scheme between active particles was implemented. This connectivity scheme allows for a more adequate representation of the electrode topology as the total surface area of the *k*-th particle,  $A_{tot,k}$ . It is comprised of two contributions:  $A_{ely,k}$  and sum  $\sum_l A_{DC,kl}$ , which cover the area that is in contact with the electrolyte and with other particles respectively. Therefore, the total surface of the *k*-th particle can be written as

$$A_{tot,k} = A_{ely,k} + \sum_{l} A_{DC,kl}.$$
 (1)

Consequently, the total flux  $j_{tot}$  also comprises contributions from the electrolyte and from other particles

$$j_{tot} = \frac{\sum_{k} A_{ely,k} j_{BV,k} + A_{DC,k} j_{DC,k}}{\sum_{k} A_{tot,k}}.$$
 (2)

The flux across the solid/electrolyte interface is modelled with the Butler–Volmer equation

$$j_{BV} = \frac{i_0}{F} \left[ \exp\left(-\frac{\alpha F}{RT}\eta\right) - \exp\left(\frac{(1-\alpha)F}{RT}\eta\right) \right], \quad (3)$$

where the exchange current density is calculated with the following expression [4]

$$i_0 = Fkc_p^{0.5} (c_{p,max} - c_p)^{0.5} c_e^{0.5}.$$
 (4)

The overpotential  $\eta$  is defined as the difference between cell potential and equilibrium potential with the additional contribution of the surface film resistance

$$\eta = (\Phi_s - \Phi_e) - (U^{ocv} - \frac{\mu}{F}) - \frac{j_{tot}A_{tot}}{V_{tot}}R_{film}.$$
 (5)

The exchange of Li between the two particles in direct contact is driven by a difference in chemical potentials between them and can be written as [7]

$$\hat{n}_{ij} \cdot j_{DC} = \frac{c_{p,max}}{RT} P(\mu_j - \mu_i).$$
 (6)

## 2.2. Particle potential model

For the LiFePO<sub>4</sub> cathode material, the single particle chemical potential can be derived from regular solution theory [8]. Regular solution theory provides the chemical potential of an active particle as a function of the spatial distribution of lithium inside the particle [9]. For the use in the multiparticle electrochemical model, the following spinodal dependency of the particle chemical potential as a function of average particle concentration was applied [6, 10]:

$$\mu = k_b T \ln\left(\frac{x}{1-x}\right) + \Omega(1-2x).$$
 (7)

This principle was first used in the multiparticle model proposed by Dreyer *et. al* [6] and it is justified by the fact that the particle overpotential during battery operation is sufficiently high to maintain the active particle in the solid solution regime [10]. Particle size influences are introduced through a regular solution parameter,  $\Omega$ , in equation 7, as introduced in Ferguson and Bazant [11], which yields different particle size dependent shapes of chemical potentials in terms of potential gaps at the spinodals.

#### 2.3. Degradation models

Solid electrolyte interphase (SEI) growth on the anode active particles represents one of the very influential degradation mechanisms that decrease the amount of cyclable lithium. The SEI growth model, based on the approach from references [12, 13], was therefore integrated in the modelling framework to highlight the capabilities of the developed modelling framework to consider back influences of the loss of cyclable Li and topological changes of the electrodes on battery performance.

The total Li molar flux to the surface of the single anode active particle is determined as a sum of two different contributions: molar flux of Li due to intercalation and due to the SEI

$$j_{TOT} = j_{BV} + j_{SEI}.$$
 (8)

 $j_{BV}$  was modelled using equation 3 [1, 14]. The flux  $j_{SEI}$  is modelled based on the Tafel equation [12] and can be written as:

$$j_{SEI} = -k_{SEI} c_{EC}^{S} \exp\left(-\frac{\alpha_{SEI} F}{RT} \eta_{SEI}\right), \quad (9)$$

where  $c_{EC}^{s}$  can be calculated from  $c_{EC}^{0}$  [12]. The overpotential  $\eta_{SEI}$  drives the SEI formation reaction and is dependent on cell potential, film resistance and SEI equilibrium potential [12].

The rate of growth of the thickness of the SEI film is proportional to  $j_{SEI}$ :

$$\frac{\partial \delta_{film}}{\partial t} = -\frac{1}{a_n} \frac{j_{SEI}}{2} \frac{M_{SEI}}{\rho_{SEI}},$$
 (10)

where the proportionality of these two parameters is influenced by particle properties i.e.  $M_{SEI}$ ,  $\rho_{SEI}$  and  $a_p$ . The thickness of the SEI film and its conductivity influence the resistance of the SEI film, which in return influences the flux equations (equation 8). This closes the system of partial differential equations for modelling SEI growth. In addition to shifting the overpotentials of the active particle, this model of the SEI formation also accounts for changes in the amount of cyclable lithium. Coupled with the electrochemical model, this SEI formation model enables the study of complex interactions between degradation, electrochemical and transport phenomena.

## 3. **RESULTS**

## 3.1. LFP half-cell with Li-metal anode

A half-cell composed of a LFP cathode, a separator and a Li-metal anode was analysed, is applied to confirm the adequacy of the proposed advanced battery modelling framework, incorporating sub-models for realistic particle size distribution, particle connectivity and particle size dependent cathode particle potential.

Figure 2 shows a comparison between experimental and modelled cathode potential at different C-rates for a half-cell. Results are shown for a 25  $\mu$ m thick electrode relying on an experimentally determined primary particle size distribution with a mean value of approximately 200 nm and 49% porosity.



Figure 2: A comparison between experimental and modelled half-cell potentials during discharge for different C-rates and different modelling representations of the electrode.

Good agreement between measured and experimental curves at low C-rates confirms the adequacy of the particle potential model (second term in equation 5) and the capability of the model to adequately simulate a slight slope of the voltage curve. This is to a large extent driven by inter-particle phase separation of the phase separating material, which is influenced by the size dependency of the particle's chemical potentials.

Another important aspect is presented in Figure 3, where the parameters of two particles in direct contact with each other are shown for a C/100 discharge. The DOD curves show a particle transition from Li-poor to Lirich phase occurring at  $x \approx 0.7$  for a smaller, and at  $x \approx 0.9$  for a larger particle. Pronounced partial cycling, which originates from interactions with other particles, is visible before the transition. The redistribution of Li between particles occurs during phase separation when a lithiating particle extracts Li from neighbouring particles, which are in direct contact with this particle and consequently lowers their DOD, and/or from the electrolyte. This phenomenon is clearly seen in the traces of Butler–Volmer fluxes,  $j_{BV}$ , and direct contact fluxes,  $j_{DC}$ , of both particles. At  $x \approx 0.7$  both  $j_{BV}$  and  $j_{DC}$  of Particle #1 reach their highest values, which results in the negative signs of fluxes of Particle #2, meaning that the fraction of Li was redistributed from Particle #2 to the lithiating Particle #1.

Furthermore, good agreement between the measured and modelled curves at high C-rates (Figure 2) additionally confirms the adequacy of the framework's modelling representation of the topology of the cathode within the proposed modelling framework. Besides the direct Li transport between particles, this modelling representation reduces the area for Li transfer across the solid/electrolyte interface (equation 1) and also

increases the losses of direct Li transport between particles, which do not have well aligned channel for fast diffusion [15]. Both effects, therefore, increase the overpotentials required to transport Li into particles which feature a small solid/electrolyte area and which are connected to other particles by not well-aligned channels for fast diffusion. This is the main mechanism for low Li utilization at high rates.



Figure 3: The Butler–Volmer and direct contact Li molar flux at the surface of the two representative particles in direct contact during a discharge cycle at C/100, where the transition from the Li-poor to the Li-rich phase can be observed from a particle's DOD curve.

Unlike materials featuring larger secondary particles, e.g. in the range of 5  $\mu$ m, featuring high level of homogeneity, where low Li utilization at high rates is indeed mainly limited by the bulk particle diffusion [16], bulk particle diffusion in small LiFePO<sub>4</sub> particles does not yield low Li utilization at high rates, as is discernible from the presented results. This is clearly seen from both curves in Figure 2, which were obtained by the model, where particles were in a full contact with the electrolyte, thus neglecting connectivity to other particles via the not well-aligned channels for fast diffusion. This modelling approach, which represents the basis of commonly applied continuum models on the level of the entire electrode [1], results in the wrong prediction of a nearly full Li utilisation at a high 5C rate (Figure 2). These results are also not influenced by the selection of a modelling approach for simulating intraparticle diffusion, as results are nearly identical for the Fickian and the fast diffusion approach. This further confirms that intra-particle diffusion is not a ratedetermining step for small particles. To compensate for this deficiency of current continuum models, some studies limit Li utilisation by the empirical distribution of resistive terms [17]. However, the SEM image in Figure 1 and previous studies, e.g. [15, 18], clearly indicate that low Li utilization at high rates is to a large extent related to the topological characteristics of the electrodes.

These results show for the first time, the significance of the electrode topology, and thus the significance of the particle size distribution and connectivity for the adequate prediction of low Li utilization in small particles at high rates. The proposed innovative modelling framework therefore represents a continuum modelling approach, enabling more consistent reproduction of real multi-particle size distributions and particle connectivity, thus enabling more consistent modelling of transport phenomena.

## 3.2. LFP full-cell with graphite anode

The modelling of the cell degradation phenomena was performed on the full cell sandwich, including the graphite anode (Figure 1). The proposed modelling framework calculates all relevant potentials, which in turn influence fluxes over the entire sandwich. These spatial and temporal stimuli form the basis for the accurate modelling of SEI growth rates (equation 9).

Figure 4 shows rates of SEI growth on three differently sized and positioned particles in the anode. The inner figure shows parameters for half of the cycle, represented with notation in the interval from 0 to 0.5, where the characteristic shape of the SEI growth during anode particle delithiation is presented [13].

The SEI degradation mechanism consumes active Li from the electrolyte, which on one hand increases the SEI related overpotential for Li transport (equation 5), and on the other hand reduces the amount of cyclable Li. It is well known [19] that over longer periods, both effects result in a reduction of the energy content of the battery. The results in Figure 5 confirm that the proposed modelling framework, which features a consistent integration of performance and degradation models of SEI formation, is capable of simulating these phenomena. Figure 5 clearly presents lower battery voltage due to increased SEI related overpotential for Li transport, and due to lower cell capacity caused by the loss of cyclable Li, in the comparison between the fresh and the cycled cell. The loss of potential is especially pronounced towards the end of discharge curve, due to the loss of cyclable lithium, which increases the potential difference of the delithiated graphite anode against the Li/Li+ potential.



Figure 4: SEI growth on the surface of three representative particles in the first fifty 1C (dis)charge cycles with a detailed view of the first discharge cycle.



Figure 5: Comparison of full cell potential for the fresh and cycled cell simulated at C/100.

## 4. CONCLUSIONS

This paper presents an innovative continuum Li-ion battery modelling framework, incorporating innovative features that allow for: a more adequate topological representation of electrodes, the calculation of particle potentials, as well as a consistent integration of performance and degradation models.

The capabilities of the modelling framework were validated on the LiFePO<sub>4</sub> cathode material, which features non-monotonous particle chemical potential as function of particle lithiation, thus being a representative of a very challenging cathode material for Li-ion battery model validation. The presented results clearly indicate that the proposed modelling framework is - compared to current state of the art - capable of more adequately modelling macroscopic and mesoscopic battery parameters. This is confirmed by the high relevance of modelled voltage vs. capacity results for low and high discharge rates and the simultaneous high relevance of interparticle transport phenomena, which are in agreement with recent nanoscopic findings. These results clearly confirm the necessity of properly considering the real topological characteristics of the

electrode in terms of real multi-particle size distributions and particle connectivity. Presented results also confirm an adequate modelling representation of interactions between degradation phenomena and the predicted voltage vs. capacity results.

The proposed modelling framework, therefore, represents significant progress in the area of model supported battery design and contributes to an in-depth understanding of the cause and effect chain from battery operation to degradation. It thus efficiently contributes to the model supported design of battery-based energy systems.

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