Thermodynamically Consistent and Computationally Efficient 0D Lithium Intercalation Model of a Phase Separating Cathode Particle

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September 26, 2019

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Abstract

A new mechanistically derived 0D model of a phase separating active cathode particle was designed for use in a multi particle porous electrode theory based model. The proposed 0D model was obtained by integration of dynamic equations of the spatially resolved single particle model, based on the regular solution theory. The described analytic procedure yields a thermodynamically consistent 0D model that preserves physicochemical relevance of the spatially resolved model and reduces computational times by up to six orders of magnitude. Besides its computational efficiency, the 0D model features high levels of consistency with the spatially resolved model in the low and high overpotential limit, which are most relevant for cell modelling. A transparent relation to the spatially resolved model provides validation of the suitability of previously applied intuitive approaches assigning spinodal average chemical potential to the entire particle. It also offers additional insights into the physicochemical phenomena inside a multiparticle electrode. The proposed 0D approach provides the basis for modelling advanced experimental observations covering: charge/discharge hysteresis, varying active particle population, solid solution vs. phase separating state of particles within active population, and memory effect when implemented in the multi particle phase separating porous electrode theory based model.
1 Introduction

A rapid increase in mobile applications has resulted in intense research on energy storage devices. Li-ion batteries are widely used due to their large capacity. However, simultaneous maximization of the energy and power densities as well as lifetime and safety of batteries calls for profound insight into the phenomenology of underlying processes, which can be provided with the advanced simulation models of the Li-ion battery cells.

Common engineering approach frequently relies on the battery cell equivalent circuit models [1] that allow for adequate reproduction of battery voltage profile during operation after models were subjected to calibration against specific experimental data. Despite their real time calculation capability, the lack of fundamental physicochemical basis of these models results in poor prediction capability of such models outside the region of calibration data, while they are, in general, also not capable of ensuring sufficient accuracy for changed cell designs and changed cell materials. In order to maximize the efficiency of Li-ion battery development process several detailed electrochemical models of the battery cell were introduced in recent years [2]. Transient simulations on the level of electrode sandwich, i.e. anode, cathode, electrolyte and separator materials, are generally performed with continuum models, which allow for obtaining insight into coupled transport, electrochemical and heat generation phenomena at the sandwich level.

Pioneering work in the field of continuum battery electrochemical modelling was published in 1975 by Newman et.al [3] under the name Porous-electrode theory. Newman approach was proven to be successful for the description of battery cell behavior and, therefore, it was extensively modified and upgraded since its creation. Porous-electrode theory is, in general, the basis for multiple electrochemical battery models (also called Newman based models) until today when it is implemented in several research codes, e.g. [4, 5, 6], and commercial software packages, e.g. [7, 8, 9].

Even though Newman based models are frequently used, they feature certain deficiencies. Concentrations and potentials of cathode and anode active particles are usually calculated by the second Fick’s law of diffusion [3, 10, 11, 12, 13, 14] and fitted voltage vs. DoD curves [10, 11, 14]. Diffusion can be modeled relatively accurately using second Fick’s law of diffusion for the single-phase solid-solution active materials (LiCoO$_2$, NMC...), whereas for the phase separating active materials (LiFePO$_4$, LiMnPO$_4$, graphite) this is not the case [5]. For phase separating materials, this simplistic approaches introduce fundamental thermodynamic inaccuracies to the model thus compromising its prediction capability and thus accuracy of the model [5].

This challenge motivated several researches on the phase separating sin-
gle particle microscale models that were published in the last decade [15, 16, 17, 18, 19, 20, 21, 22, 23, 24]. Precise single particle models of the phase separating material are namely crucial for plausible determination of particle potentials that inherently influence transport processes. However, in real continuum model applications, objective on high accuracy of the single particle model needs to be balanced with the computational effort of such a model to ensure acceptable computational times of the continuum model.

Pioneering work in the explaining the origin of hysteresis in insertion batteries composed of phase separating material was proposed by Dreyer et. al [25], where particles are represented as 0D points with the prescribed chemical potential as a function of state of charge. Despite local nature of the chemical potential inside a particle, authors succeeded to provide inspiring phenomenological explanation of the particle by particle lithium exchange (also called mosaic or balloon model) using spinodal curve as representative for the average chemical potential of the entire particles. Similar, particle averaged, approach for the shape of the chemical potential was applied by Sasaki et. al [26] to explain memory effect in LiFePO$_4$, while Kondo et. al [27] later published a more consistent explanation of the memory effect again relying on the particle averaged approach. All cited references, thus, report multiparticle electrode model relying on 0D active particles approach with spinodal average chemical potential, which was assigned to the entire entire particle.

Additionally, in reference [26] authors indicated that other shapes of dependencies of the average chemical potential on state of charge are also possible a in 0D modelling representation of an active particle. In addition to a spinodal shape of the chemical potential at high overpotentials, reference [26] provides correct intuitive explanation that particles follow two phase equilibrium chemical potential curve at very slow (near equilibrium) battery charge/discharge, which has a shape of a plateau. These intuitive indications on average chemical potential shape from references [26] were justified by Bai et. al [16] who simulated the shape of average chemical potential by a detailed one dimensional single particle model. Even though recent literature indicated that boundary condition of the one dimensional single particle model in reference [16], which was used to generate reported results, was oversimplifie [20, 28, 29], fundamental physicochemical processes were consistently included in bulk dynamic, which ensured correct trends of simulated results. Results of the one dimensional single particle model [16] namely show that high interfacial current (high overpotential) across the particle surface leads to the spinodal shape of average chemical potential, whereas at low interfacial current (low overpotential) the plateau shape is observed. Results of this one dimensional model were afterwards used as parameterized inputs of
the shape of average chemical potential in a multiparticle model with 0D particles, which successfully showed transition from particle by particle to concurrent intercalation in the phase separating electrode (Li et. al [30]). Despite inspiring results and insightful phenomenological explanations, current literature does not offer a clear mechanistically based justification of the shape of the average chemical potential of the entire particle for phase separating materials.

To present an addition advance in the area of enhancing prediction capability of continuum models for batteries comprising phase separating materials, average chemical potential of the entire particle for phase separating materials was analytically derived by consistent dimension order reduction of a spatially resolved phase separating single particle model to 0D. Dimension order reduction is performed based on the spatially resolved single particle model presented in reference [29]. Mechanistically derived 0D model derived from a thermodynamically consistent spatially resolved parent model [29] provides analytic, unequivocal proof on suitability of previously applied intuitive approaches assigning spinodal average chemical potential of a phase separating material to the entire particle [25, 26, 27], while it also offers additional insights in to physicochemical phenomena inside a multiparticle electrode. A novel dimension order reduction of phase separating single particle model to 0D, being demonstrated on the phase separating LiFePO₄ material, is characterized by the following features:

- It relies on spatially resolved model [29], which is mechanistically derived from the regular solution theory and, therefore, offers thermodynamically consistent basis for the dimension order reduction.

- It is consistently derived from the parent model by volume integration (averaging) of dynamic system of equations governing lithium concentration and chemical potential in an active particle providing reasoning on the applicability of a 0D particle model for modern ultrafine powder LiFePO₄ materials [31].

- It offers a mechanistically derived explicit equation for the particle chemical potential that depends on particle state of charge, direction of intercalation current (i.e. charging or discharging), particle overpotential, particle size and particle shape.

- It provides a direct input of the particle potentials in multiparticle models in a form of an explicit equation and it, therefore, ensures computational times reduction in the range of six orders of magnitude compared to spatially resolved single particle models, e.g. [29].
• It is capable of reproducing several phenomena predicted by previously published spatially resolved single particle models i.e. Chan - Hilliard regular solution model [32, 33, 34, 35], domino cascade two phase model [36, 37], suppression of phase separation [16], particle size and shape dependency [38, 20, 28].

• It offers adequate basis for prediction of the battery cell charge/discharge hysteresis [25] and of the active particle population for particles in the solid solution and particular in the phase separated regime [39, 30].

2 Active Particle in Porous Electrode Theory

Porous electrode theory as presented in references [3, 11, 12] consist of four partial differential equations that are obtained from mass and charge conservation laws coupled together by boundary conditions. Mass conservation in the active material provides dynamic equation that defines spatial and temporal dependency of lithium concentration (molarity) inside the active particle. Mass conservation equation in its most general form can be written as:

$$\frac{\partial c}{\partial t} = \nabla \cdot \left( \frac{Dc}{k_bT} \nabla \mu \right).$$

(1)

Proportionality between flux and gradient of chemical potential is applied at the surface of the particle (active material/electrolyte interface) as boundary condition for Equation 1:

$$\frac{Dc}{k_bT} \nabla \mu = j.$$

(2)

Interfacial current $j$ is frequently modeled by a Butler-Volmer equation and reads:

$$j_{BV} = j_0 \left[ \exp \left( \frac{\alpha z F}{RT} \eta \right) - \exp \left( \frac{(1 - \alpha) z F}{RT} \eta \right) \right],$$

(3)

whereas other forms of equations for modelling interfacial current were also published, e.g. [40, 41, 42]. Derived 0D model is independent of the formulation of the equation for modelling interfacial current. $j$ is mainly influenced by $\eta$ being an overpotential that is defined as

$$\eta = \phi_s - \phi_e - \left( U_{OCV} - \frac{\mu}{e_0} \right).$$

(4)

System of equations is complete by definition of chemical potential of active particles, $\mu$, that governs intra particle concentration dynamics and transport of lithium across the particle surface and explicitly enters equations 1,
2 and 4. Equations 1, 2, 3 and 4 together with dependency of the chemical potential, $\mu$, on concentration, $c$, represent a single particle intercalation model. For the description of phase separating intercalation particle, two common approaches exist for the determination of the dependency of chemical potential, $\mu$, on concentration, $c$.

### 2.1 Ideal Solution Chemical Potential

A standard approach follows ideal solution theory for the determination of dependency of inter particle chemical potential on lithium concentration [11, 12], where Nernst equation [43] is used for the relation between $\mu$ and $c$. Nernst relation transforms Equation 1 to the form of second Fick’s law of diffusion

$$ \frac{\partial c}{\partial t} = D \nabla^2 c. \quad (5) $$

Equation 5 is easy to solve and does not increase the computational demand of the whole porous electrode model. Nevertheless for the precise description of phase separating active material this model meets serious limitations. It is possible to overcome this limitations by introduction of open circuit voltage $U_{OCV}$ as fitting parameter, added to $\mu$ in the equation 4, which ensures good match between measured and modeled charge and discharge curves of the battery cell, modeled by porous electrode theory, e.g. [10, 11, 14]. However, fitting procedure compromises prediction capability of such a model. This deficiency can be greatly improved if the regular solution is used for the description of active material instead of the ideal solution.

### 2.2 Regular Solution Chemical Potential

Detailed single particle models of phase separating electrode active particles rely on the regular solution theory for the determination of $\mu(c)$ as a function of particle lithiation [32]

$$ \mu = \mu_0 + k_b T \ln \left( \frac{c}{c_m - c} \right) + \Omega \left( 1 - \frac{2c}{c_m} \right) - \frac{\kappa V_s}{c_m} \nabla^2 c, \quad (6) $$

which significantly improves physical accuracy of the model. Inserting $\mu(c)$ from Equation 6 into Equation 1 results in Cahn - Hilliard equation [32]

$$ \frac{\partial c}{\partial t} = \frac{D}{k_b T} \nabla \cdot \left[ c \left( k_b T \frac{c_m}{c(c_m - c)} \nabla c - \frac{2\Omega}{c_m} \nabla c - \frac{\kappa V_s}{c_m} \nabla^3 c \right) \right]. \quad (7) $$

Cahn - Hilliard equation (Equation 7) adequately describes several complex phenomena, as for example uphill diffusion, spinodal decomposition and formation of diffusive phase boundary, that were observed in phase separating
active cathode particles [16, 36, 29]. Despite its merits is not feasible to use such an equation in the multiparticle porous electrode theory based models due to very significant computational demand to solve fourth order and non linear Equation 7 even for a single particle.

3 Derivation of 0D Single Particle Model

Therefore, a new single particle model was derived, which combines physicochemical accuracy of the regular solution approach (Equation 7) in most relevant overpotential regimes and very low computational demand. Therefore, newly derived model is suitable for the use in multiparticle porous electrode theory based models. Due to the fact that solving Equation 1 on the particle with spatial resolution for any $\mu(c)$ apart from ideal solution is computationally to demanding for multiparticle model, dimensionality of particles was reduced to zero. Such a reduction is possible because in the envisaged modelling depth only surface (not bulk) chemical potentials of the particles are important for physicochemical consistent description of transport and electrochemical phenomena in the porous electrode theory based model. 0D representation namely implies the use of averaged quantities (average concentration, $\bar{c}$, and average chemical potential, $\bar{\mu}$), since spatial resolution was omitted. Derivation of proposed 0D model is inspired by several different already existing approaches and by previously observed experimental or theoretical phenomena. The main foundation of the new 0D model is our, previously published, spatially resolved quasi 2D regular solution theory based model presented in reference [29] and innovative systematic two step procedure of averaging (concentration and chemical potential averaging) as well as consideration of particle size and shape.

3.1 Concentration Averaging

Equations 1 and 2 are significantly simplified in averaged (0D) representation, which is obtained by volume integration of Equation 1:

$$\int_{V_p} \frac{\partial c}{\partial t} dV = \int_{V_p} \nabla \cdot \left( \frac{D c}{k_b T} \nabla \mu \right) dV. \quad (8)$$

Left hand side of the Equation 8 can be transformed using Leibniz integral rule [44], which ensures that integral and partial differential operators on the left hand side of Equation 8 can be interchanged, resulting in a time
derivation of the average concentration

\[ \int_{V_p} \frac{\partial c}{\partial t} dV = \frac{\partial}{\partial t} \int_{V_p} c dV = V_p \frac{\partial \bar{c}}{\partial t}. \]

**Right hand side of the Equation 8** was averaged by use of Divergence theorem to transform volume integration to integration across particle surface. Conditions at the surface are described by the boundary condition in Equation 2, which can be used to further simplify right hand side of Equation 8

\[ \int_{V_p} \nabla \cdot \left( \frac{D_c}{k_b T} \nabla \mu \right) dV = \oint_{A_p} \frac{D_c}{k_b T} \nabla \mu dA = \oint_{A_p} j dA = j A_p. \]

Temporal dependency of average concentration is governed only by conditions at the surface, independent of bulk, enabling derivation of the final expression, which governs temporal dependence of the average concentration, in the 0D representation:

\[ \frac{\partial \bar{c}}{\partial t} = \frac{A_p}{V_p} j. \] (9)

Complexity of obtained Equation 9 is much lower in comparison to Equation 1, which it replaces. Beside that Equation 2 was eliminated since boundary condition is already integrated in Equation 9 and it is no longer needed. Not only that total number of equations was reduced by one, the main advantage of newly obtained system of equations is the fact that chemical potential of the active material, \( \mu \), explicitly enters only definition of the overpotential (Equation 4) in a linear form. No model relevant equation, therefore, includes gradient of the chemical potential of a particle. This enables the simple use of prescribed functional dependency of chemical potential, \( \mu \), on average concentration, \( \bar{c} \), during simulation, which drastically decrease computational time.

Besides mathematical reasoning of the averaging approach, it is also important to highlight a material and material processing related reasoning of such an approach. Despite the fact that spatially resolved particle models are generally used in the continuum battery models, i.e. most commonly in the form of a spherical diffusion equation [3, 10, 11, 12, 13, 14], it is possible to use a 0D approach for the LiFePO\(_4\) material. This is reasoned by the fact that modern LiFePO\(_4\) materials feature particles in the size range of 100 nm with fast diffusion in 010 crystallographic direction [31, 45] and thus characteristic times for diffusion are in the range of milliseconds as reported in [16]. This result is consistent with results of a quasi 2D model [29] when using commonly reported diffusion coefficients [46, 47], whereas also with
very low diffusion coefficients of $10^{-12} \text{ cm}^2/\text{s}$ and $10^{-13} \text{ cm}^2/\text{s}$ in reference [16], characteristic times are in the range of 1 minute [16]. Unlike, in multiple other materials, e.g. NMC, secondary particles, which frequently feature spherical shapes and very low intra secondary particle electrolyte concentrations, are much larger, e.g. several micrometers, and, therefore, they feature much longer characteristic times for diffusion, which scale with $R^2$, thereby implying the use of spatially resolved particle models.

3.2 Chemical Potential Averaging

The missing part to enclose a newly derived system of 0D model equations (Equations 3, 4 and 9) is averaged chemical potential that enters Equation 4. Chemical potential, $\mu$, can not be explicitly, unambiguously written as a function of average concentration, $\bar{c}$. In general, a full spatially resolved model is needed for a precise evaluation of a chemical potential (Equation 10), whereas a methodology to overcome this deficiency by averaging chemical potential $\mu$ under preservation of physical relevance and minimal loss of calculation precision is proposed subsequently.

Derivation of an expression defining dependence of the chemical potential on concentration (Equation 6) to obtain average chemical potential as a function of average concentration follows a similar approach as presented in Section 3.1:

$$\bar{\mu} = \frac{1}{V} \int_{V_p} \mu dV = \mu_0 + k_b T \int_{V_p} \ln \left( \frac{c}{c_m - c} \right) dV + \Omega \left( 1 - \frac{2\bar{c}}{c_m} \right) - \frac{\kappa V_s}{c_m} \int_{V_p} \nabla^2 c dV. \quad (10)$$

Logarithmic and gradient penalty term in Equation 10 can not be explicitly expressed as a function of average concentration $\bar{c}$. Explicit dependency of average chemical potential, $\bar{\mu}$, on average concentration, $\bar{c}$, was, therefore, derived from Equation 10 in two limiting cases: limit of high and low overpotentials.

Relevance of addressed overpotential limits can be reasoned by the fact that active particles of a battery under the normal condition of operation are subjected to much higher overpotentials than 40 mV, meaning that high overpotential limit is realized during normal operation of a battery [16]. On the other hand, in the open circuit constellation active particles relax back to the thermodynamic equilibrium, i.e. low overpotential limit.
3.2.1 High Overpotential Limit

The first limiting case refers to high overpotentials, $\eta$ (high current densities across particle surface $j$), where chemical potential, $\mu$, is nearly constant due to effect of phase separation suppression that was theoretically [16] and rigorously experimentally [48] proven. No phase separation occurs at that regime and particle concentration is changed homogeneously in the solid solution manner [16, 29]. In this limiting case, constant concentration, $c$, in particle at any time enables integration of the logarithm term in Equation 10, since $\int_{V_p} \ln \left( \frac{c}{c_m-c} \right) dV = V_p \ln \left( \frac{\bar{c}}{c_m-\bar{c}} \right)$. Gradient penalty term vanishes due to constant $c$ and consequently zero concentration gradient. Dependency of average chemical potential, $\bar{\mu}$, on average concentration, $\bar{c}$, can in high overpotential limit (solid solution regime) be written in the form of the spinodal curve:

$$\bar{\mu}_H = \mu_0 + k_BT \ln \left( \frac{\bar{c}}{c_m-\bar{c}} \right) + \Omega \left( 1 - 2\frac{\bar{c}}{c_m} \right).$$

(11)

Chemical potential in high overpotential limit $\bar{\mu}_H$ is independent of the direction of interfacial current $j$ and is, therefore, the same for battery charging and discharging (lithium de-intercalation and intercalation). Such a particle model thus enables modelling charge-discharge hysteresis [25] when inserted in a multiparticle model.

3.2.2 Low Overpotential Limit

The second limiting case where dependency $\bar{\mu}(\bar{c})$ can be analytically derived is the regime of very low overpotentials, $\eta$. In this limiting case chemical potential features a near constant spatial distribution [29], due to the proximity of the thermodynamic equilibrium. Pure phase separation of the active particle occurs in this regime. The shape of averaged chemical potential at this low overpotential limit depends on cell discharging or charging (lithium intercalation or de-intercalation).

Battery Discharging (lithium intercalation)

During battery discharging lithium is intercalated into the cathode active particles. At the low concentrations (below $c^s_1$ - spinoidal point - Figure 1), particle follows solid solution regime and concentration is homogeneously increased. In this region intercalation process is identical to the one described in high overpotential limit section and thus identity $\int_{V_p} \ln \left( \frac{c}{c_m-c} \right) dV = V_p \ln \left( \frac{\bar{c}}{c_m-\bar{c}} \right)$ applies. After concentration $c^s_1$ (Figure 1) is reached instant
phase separation occurs, which results in appearance of Li-poor (FePO$_4$) and Li-rich (LiFePO$_4$) domains inside a single particle [48].

Due to a finite temperature, some amount of lithium is still present in the Li-poor phase as interstitial impurity and some lithium vacancies are present in the Li-rich phase. Equilibrium concentrations of both phases are not equal to 0 and $c_m$ but slightly changed (denoted as $c_\alpha$ and $c_\beta$ - Figure 1). By minimization of the free energy, both equilibrium concentrations $c_\alpha$ and $c_\beta$ can be calculated as root of the spinodal curve

$$k_bT \ln \left( \frac{c_{\alpha,\beta}}{c_m - c_{\alpha,\beta}} \right) + \Omega \left( 1 - \frac{2c_{\alpha,\beta}}{c_m} \right) = 0. \quad (12)$$

Right-hand side of Equation 10 can now be written as a sum of integrals over the volumes of two phases ($V_\alpha$ and $V_\beta$) and volume of phase boundary between them ($V_\lambda$):

$$\bar{\mu} = \mu_0 + k_bT \int_{V_\alpha} \ln \left( \frac{c_\alpha}{c_m - c_\alpha} \right) dV + k_bT \int_{V_\beta} \ln \left( \frac{c_\beta}{c_m - c_\beta} \right) dV +$$

$$+ V_\alpha \Omega \left( 1 - \frac{2c_\alpha}{c_m} \right) + V_\beta \Omega \left( 1 - \frac{2c_\beta}{c_m} \right) +$$

$$+ k_bT \int_{V_\lambda} \left[ \ln \left( \frac{c}{c_m - c} \right) + \Omega \left( 1 - \frac{2c}{c_m} - \frac{\kappa V_\lambda}{c_m} \nabla^2 c \right) \right] dV. \quad (13)$$

Taking into account Equation 12 and the fact that Li-rich and Li-poor phase at equilibrium occupy the same value of chemical potential yields average chemical potential $\bar{\mu} = 0$. Intuitively this can easily be understood, since both phases meet at the same chemical potential at equilibrium, otherwise flux from one phase to another would establish. Since equilibrium concentration at the minimums of free energy coincides with the roots of chemical potential, the values of chemical potentials in both phases at equilibrium must equal zero and consequently its average also equals zero. Chemical potential, $\bar{\mu}$, remains zero during slow discharge (domino cascade model [36, 29]) until particle average concentration, $\bar{\bar{c}}$, meets equilibrium value of Li-rich phase ($c_\beta$). From this point only one phase is present in the particle and solid solution regime equation $\int_{V_p} \ln \left( \frac{c}{c_m - c} \right) dV = V_p \ln \left( \frac{\bar{\bar{c}}}{c_m - \bar{\bar{c}}} \right)$ applies once again. For the whole process of discharge, average chemical potential $\bar{\mu}_{L}^{dch}$ can, therefore, be written as a piecewise function of three contributions:

$$\bar{\mu}_{L}^{dch} = \mu_0 + \begin{cases} k_bT \ln \left( \frac{\bar{\bar{c}}}{c_m - \bar{\bar{c}}} \right) + \Omega \left( 1 - \frac{2\bar{\bar{c}}}{c_m} \right) ; & \bar{\bar{c}} \leq c_1^s \smallskip \\
0 ; & c_1^s < \bar{\bar{c}} \leq c_\beta \smallskip \\
k_bT \ln \left( \frac{\bar{\bar{c}}}{c_m - \bar{\bar{c}}} \right) + \Omega \left( 1 - \frac{2\bar{\bar{c}}}{c_m} \right) ; & \bar{\bar{c}} > c_\beta \end{cases} \quad (14)$$
Dependency of the average chemical potential on average concentration in the regions of the low and high concentrations is exactly the same as in the limit of high overpotential. The difference from high overpotential limit is obtained in the intermediate range of the average concentrations, where long plateau at $\bar{\mu} = 0$ is obtained for the low overpotential limit during discharge (Figure 1).

**Battery Charge (lithium de-intercalation)**

During battery charging lithium is de-intercalated from the cathode active particles. In the limit of low overpotentials de-intercalation process follows the mirrored path of the discharge (intercalation) process. At the beginning and at the end of the charging process battery is in the solid solution regime (Equation 11 applies) and in the intermediate region plateau regime is realized due to the same arguments as in the case of the low overpotential discharging (Equation 13). The crucial difference between charging and discharging regime are the points where phase separation is initiated and the points where single phase regime is met once again (beginning and end of plateau). In the case of charging this occurs at the second spinodal concentration $c_2^s$ and Li-poor phase equilibrium concentration $c_\alpha$ (Figure 1). The final equation defining the average chemical potential during low overpotential charging can again be written as piecewise function:

$$
\bar{\mu}_L^{ch} = \mu_0 + \begin{cases} 
  k_B T \ln \left( \frac{\bar{c}}{c_m - \bar{c}} \right) + \Omega \left( 1 - \frac{2\bar{c}}{c_m} \right); & \bar{c} \leq c_\alpha \\
  0; & c_\alpha < \bar{c} \leq c_2^s \\
  k_B T \ln \left( \frac{\bar{c}}{c_m - \bar{c}} \right) + \Omega \left( 1 - \frac{2\bar{c}}{c_m} \right); & \bar{c} > c_2^s
\end{cases} 
$$

which is very similar to the $\bar{\mu}_L^{dch}$ except for the boundaries of each region of a piecewise function (Figure 10).

### 3.3 Particle Size and Shape

References [38, 20, 28] show that particle size distribution in multi-particle model is crucial for consistent description of the porous electrode. Even though it seems like reduction of dimensionality and negligence of particle spatial resolution exclude particle size from the proposed 0D single particle model, it was introduced to the chemical potential via particle size dependent parameter $\Omega$. Experimental observations as well as theoretic predictions show that phase separation is not pronounced in small particles [28]. This fact was introduced to the 0D model by determination of dependency of parameter $\Omega$ on particle size $L$, that ensures no phase separation for smaller particles.
Figure 1: Two phase equilibrium vs. solid solution chemical potential.

Dependency $\Omega(L)$ was determined for the LiFePO$_4$ particles of the C3 shape \cite{49}, which is a realistic particle shape in LiFePO$_4$ cathodes. Derivation was inspired by work presented in references \cite{38, 20, 28}. Potential barrier for the phase separation initiation, $\Delta \phi$, in LiFePO$_4$ material was measured by several authors \cite{50, 51, 52, 53, 54, 25} and theoretically described with high precision by Cogswell and Bazant \cite{28}. They showed that potential barrier for nucleation decreases near linearly with the inverse particle size $L$. $L$ represents the longest diameter of the C3 shape particle and can be expressed as $L = 3.6338 \frac{V_p A_p}{p}$, $V_p$ being particle volume and $A_p$ particle total surface area. Dependency of $\Delta \phi(L)$ as predicted in reference \cite{31} can be written as:

$$\Delta \phi = \frac{-31.4435 k_b T \text{nm}}{L} + 1.42925 k_b T.$$ \hspace{1cm} (16)

Taking into account the fact that nucleation potential barrier $\Delta \phi$ must equal half of difference between chemical potential at the spinodal points \cite{31} gives:

$$\frac{-31.4435 k_b T \text{nm}}{L} + 1.42925 k_b T = \sqrt{\Omega(\Omega - 2k_b T)} + k_b T \ln \left( \frac{\Omega - \sqrt{\Omega(\Omega - 2k_b T)}}{2k_b T} - 1 \right). \hspace{1cm} (17)$$
Right-hand side of the Equation 17 was obtained as a difference between two chemical potentials evaluated at roots of derivatives of the spinodal curve (difference between maximum and minimum of spinodal curve). This consistently analytically derived Equation 17 is similar but not fully identical to the corresponding equation in reference [31]. Equation 17 was solved numerically to obtain $\Omega(L)$. The significance of equation 17 is illustrated in Figures 2 and 3. Figure 2 shows obtained dependency of the regular solution parameter $\Omega$ on particle size $L$. Figure 3 shows the shapes of spinodal curve (Equation 6) for different particle sizes, where regular solution parameters $\Omega$ are obtained from equation 17 for each particle size presented in figure.

![Figure 2: Regular solution parameter $\Omega$ dependency on particle size $L$.](image)

Particles smaller than 22 nm do not undergo phase separation but stay in the solid solution regime across the whole state of charge range [31]. This fact is covered in Equation 17 by the fact that real solutions of this equation do not exist for particle sizes under 22 nm. Therefore, the value of the regular solution parameter $\Omega$ is set 0 for all particles smaller that 22 nm. Thereby, Equation 7 transforms to a much simpler form of $\frac{\partial c}{\partial t} = D \nabla \cdot \left( \frac{c_m}{c_m-c} \nabla c \right)$. This equation ensures solid solution regime across whole particle state of charge (SoC) regardless of the overpotential but it still differs from the classic Fick’s diffusion (Equation 5) due to the fact that maximal concentration, $c_m$, can not be exceeded.
4 Results and Discussion

Validity of the proposed 0D model is shown by comparing results of the proposed 0D model (Equation 11 and 14) to the results of the simulation conducted by a thermodynamically consistent spatially resolved model [29]. In the later model, Cahn-Hilliard equation (Equation 7) was solved on quasi 2D domain as described in paper [29]. From spatially resolved simulation results, average chemical potential dependency on average concentration was calculated in post-process. Comparison of the results is shown in Figures 4 and 5.

Simulations were performed at overpotentials $\eta = 40 \text{ mV}$ (Figure 4) and $\eta = 2 \text{ mV}$ (Figure 5). Very good agreement between the results of the quasi 2D model and proposed 0D model confirms that practically no precision was lost due to chemical potential averaging (Equation 10) in both limiting case of the applied overpotentials in nearly entire range of lithiation. The only notable deviation of the proposed 0D model from quasi 2D simulation result can be seen in at the low overpotential limit, where quasi 2D model predicts collision of the intercalation waves [19, 16, 29] yielding a decrease in $\bar{\mu}$ at high concentrations, which qualitatively does not affect multi particle dynamics. Another very important results which is inherently related to a simple explicit formulation of the 0D model arises from a very significant computational time reduced of the newly derived 0D model that is six orders of magnitude shorter.
Figure 4: Comparison between results of the quasi 2D model [29] and proposed 0D model (Equation 11). Dependency of average chemical potential, $\bar{\mu}$, on the amount of lithium inside a particle (average concentration $\bar{c}$) in high overpotential limit at 40 mV.

Applicability of the proposed 0D model is not impaired by omission of the intermediate region between both overpotential limit represented in Figures 4 and 5. This can be reasoned by the fact that active particles of a battery under the normal condition of operation are subjected to much higher overpotentials than 40 mV, meaning that high overpotential limit is realized during normal operation of a battery [16]. On the other hand, in the open circuit constellation active particles relax back to the thermodynamic equilibrium. Most of the time during relaxation process, active particles are near thermodynamic equilibrium, which makes low overpotential limit applicable for the description of such a relaxation. Since active particles of the battery in standard operation applications are rarely found in the intermediate range between high and low limit the model can be reduced to those two limits only without compromising prediction capability and physicochemical accuracy of the model.

Mechanistically accurate representation of active particles in the presented 0D model provides the basis for modelling of advanced physicochem-
Figure 5: Comparison between results of the quasi 2D model [29] and proposed 0D model (Equation 14). Dependency of average chemical potential, $\bar{\mu}$, on the amount of lithium inside a particle (average concentration $\bar{c}$) in low overpotential limit at 2 mV.

Theoretical findings when integrated in a multi particle phase separating porous electrode theory based model:

1. Obtained shapes of chemical potential in both overpotential limits (Equations 11, 14 and 15) inherently enable modelling of charge/discharge curve hysteresis if implemented in a multiparticle model. Non monotony and existence of local extremes in the low overpotential limit of a chemical potential (equations 14 and 15) namely provide the basis for modelling of a charge/discharge hysteresis featuring thermodynamic origin at very low currents [25]. These findings are also in line with the latest experimental observations [39], which shows that particles follow the phase separated path during slow (near equilibrium) charge/discharge.

2. Reference [30] provides theoretical and experimental evidence that active particle population in the phase separating cathodes is strongly influenced by discharging C rate and can be as high as 80% in some cases. Further, reference [39] shows, that particles within large active particle population can be found also in the phase separated state.
Proposed 0D model provides the basis for modelling both phenomena. Large active particle populations of the particles in phase separated state are namely the consequence of plateau in Figure 5 being at the same value of the chemical potential as the equilibrium concentrations $c_\alpha$ and $c_\beta$ (Figure 1), which makes inter-particle phase separated active population stable.

3. Proposed 0D model incorporates size dependent potential barrier for phase separation initiation ($\Delta \phi$) (Figure 2). Consequently intercalation in smaller particles is faster in comparison to intercalation in large particles if exposed to the same conditions. This feature of the proposed model provides the basis for the simulation of memory effect described in references [26, 27].

5 Conclusions

A 0D model of the cathode phase separating active particle was derived by the innovative approach relying on dimensionality order reduction of a thermodynamically consistent spatially resolved model [29]. Besides mathematical reasoning on the suitability of the 0D approach for modelling active LiFePO$_4$ particles, a material and material processing reasoning being based on characteristic times of diffusion in modern ultrafine powder LiFePO$_4$ materials is also provided. Proposed dimensionality reduction procedure is based on the volume integration (averaging) of dynamic equations of spatially resolved model and consists of two steps: concentration and chemical potential averaging. Resulting 0D model is characterized by explicit dependency of the average chemical potential on state of charge of the entire particle composed of a phase separating material. It is therefore of a great advantage for application in multiparticle porous electrode models, as it features very short computational times and high level of consistency with a parent model in low and high overpotential limit, which are most relevant for cell modelling.

Consistent analytic dimensionality order reduction from the spatially resolved parent model provides validation on suitability of previously applied intuitive approaches assigning spinodal average chemical potential of a phase separating material to the entire particle by parameterization through spatially resolved models [39] or intuitively constructed average chemical potentials of the entire particle [25, 26]. Consistent analytic dimensionality order reduction offers also additional insights into physicochemical phenomena inside a multiparticle electrode and provides the basis for modelling of advanced experimental observation covering charge/discharge hysteretic, varying active
particle population in the electrode, solid solution vs. phase separating state of particles inside active population and memory effect when implemented in a multi particle phase separating porous electrode theory based model. It can thus be concluded that proposed thermodynamically consistent and computationally efficient 0D lithium intercalation model presents an addition advance in the area of enhanced prediction capability of continuum models for batteries comprising phase separating materials.
# List of Symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Meaning</th>
<th>Units</th>
</tr>
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<tbody>
<tr>
<td>$A_p$</td>
<td>active particle surface area</td>
<td>m²</td>
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<tr>
<td>$\alpha$</td>
<td>charge transfer coefficient</td>
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<tr>
<td>$c$</td>
<td>lithium molar concentration</td>
<td>mol/m³</td>
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<tr>
<td>$\bar{c}$</td>
<td>average lithium molar concentration</td>
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<td>$c_{\alpha}$</td>
<td>Li-poor phase equilibrium Li concentration</td>
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<td>$c_{\alpha,\beta}$</td>
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<td>Li-rich phase volume</td>
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</table>
\(V_\Lambda\) Li-rich/Li-poor interphase volume \(m^3\)

\(V_p\) active particle volume \(m^3\)

\(V_s\) intercalation site volume \(m^3\)

\(\Omega\) regular solution parameter eV

\(z\) charge number 

**Acknowledgements**

The authors acknowledge financial support from the Slovenian Research Agency (research core funding No. P2-0401) as well as the project Next-generation electrochemical LiFePO\(_4\) battery model, ID J7-8270, which is also financially supported by the Slovenian Research Agency.

**References**


