A computational homogenization approach for Li-ion battery cells.  

Part 1 - Formulation

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Abstract

Very large mechanical stresses and huge volume changes emerged during intercalation and extraction of Lithium in battery electrodes. Mechanical failure is responsible for poor cyclic behaviors and quick fading of electrical performance, especially in energy storage materials for the next generation of Li-ion batteries. A multi scale modeling of the phenomena that lead to mechanical degradation and failure in electrodes is the concern of the present publication. The computational homogenization technique is tailored to model the multi physics events that coexist during batteries charging and discharging cycles. At the macroscale, diffusion-advection equations model the coupling between electrochemistry and mechanics in the whole cell. The multi-component porous electrode, diffusion and intercalation of Lithium in the active particles, the swelling and fracturing of the latter are modeled at the micro-scale. A rigorous thermodynamics setting is stated and scale transitions are formulated.

1 Notation

1.1 Symbols and operators
- the symbol $\mathds{1}$ denotes the identity matrix  
- the symbol $\text{Tr}[-]$ denotes the trace operator  
- the symbol $\text{Dev}[-]$ denotes the deviator operator  
- the symbol $\text{div}[-]$ denotes the divergence operator  
- the symbol $\nabla [-]$ denotes the gradient operator  
- the symbol $\Delta [-]$ denotes the Laplace operator  
- the symbol $||x||^2 = x \cdot x$ denotes the squared norm of vector $x$, with $\cdot$ scalar product  
- the symbol $\mathbf{e}_j$ with $j \leq n$ denotes the $j^{th}$ unit vector of the canonical basis for $\mathbb{R}^n$

1.2 Subscripts and apexes
- the subscript $a$ identifies quantities in the active particles, thus at the micro scale only  
- the subscript $c$ identifies quantities in the conductive particles, thus at the micro scale only  
- the subscript $e$ identifies quantities in the electrolyte, at both scales  
- the subscript $\text{e}$ identifies quantities for electrons, at both scales  
- the subscript $\text{Li}^+$ identifies quantities for Lithium cations, at both scales  
- the subscript $\text{X}^-$ identifies quantities for anions, at both scales  
- the subscript $\text{Li}$ identifies quantities for neutral Lithium, at both scales  
- the subscript $\mathcal{E}$ identifies quantities in the electrode, thus at the macro scale only  
- the apex $^m$ identifies quantities at the micro scale only.  
- the apex $^M$ identifies quantities at the macro scale only.

1.3 Variables and fields
- $\mathbf{b}$ denotes the body force vector  
- $c$ denotes the concentration measure called molarity, moles per unit volume
- \( c_{a}^{\text{max}} \) denotes the saturation limit for Lithium in the active particles material
- \( D \) denotes the diffusivity coefficient
- \( D_{ij} \) denote the Maxwell-Stefan diffusivities
- \( E \) denotes electric field
- \( f_{a} \) denotes the activity coefficient of species \( \alpha \)
- \( f_{\pm} \) denotes the mean activity coefficient for a dissolved salt
- \( G \) denotes the shear modulus
- \( h_{a} \) denotes the the mass flux of species \( \alpha \), the number of moles of species \( \alpha \) per unit area per unit time
- \( i_{a} \) denotes the mass supply of species \( \alpha \), the number of moles of species \( \alpha \) per unit volume per unit time
- \( i \) denotes the charge supply (in coulombs per unit volume per unit time)
- \( i_{0} \) denotes the exchange current density in the Butler-Volmer interface conditions
- \( I \) steady given current density in a galvanostatic process
- \( K \) denotes the bulk modulus
- \( M \) denotes the mobility tensor
- \( M_{0} \) denotes the mobility constant
- \( n \) denotes the outward normal direction on a surface
- \( q \) denotes the heat supplied by external agencies
- \( q \) denotes the heat flux vector
- \( t \) denotes time
- \( t_{Li^{+}} \) denotes the transference (or transport) number of \( Li^{+} \) ions in the solution
- \( u \) denotes the specific internal energy
- \( u_{a} \) denotes the \( \alpha \)-ion mobility
- \( V \) denotes a domain at the microscale
- \( \dot{\partial}V \) denotes a boundary or an interface between domains at the micro scale
- \( y \) denotes the set of variables that model driving forces
- \( z_{a} \) denotes the valency of ion \( \alpha \)
- \( \beta \) denotes the symmetry factor in the Butler-Volmer interface conditions
- \( \gamma \) denotes the thermodynamic imbalance at electrode-electrolyte interface
- \( \Gamma \) denotes a boundary or an interface between domains at the macro scale
- \( \epsilon \) denotes the porosity
- \( \varepsilon \) denotes the small strain tensor
- \( \zeta \) denotes the charge density, in coulombs per unit volume
- \( \eta \) denotes the specific entropy
- \( \vartheta \) denotes the absolute temperature
- \( \kappa \) denotes the conductivity
- \( \lambda \) denotes the Lamè elastic modulus
- \( \mu \) denotes the chemical potential, also known as partial molar free energy
- \( \Pi \) denotes the electrochemical potential
- \( \mu_{0} \) denotes the reference value of the chemical potential of the diffusing species
- \( \rho \) denotes the mass density
- \( \xi \) denotes the discontinuity for the electrostatic potential
- \( \sigma \) denotes the Cauchy stress tensor
- \( \phi \) denotes the electric potential
- \( \Phi \) denotes the Grand or Landau potential
- \( \chi \) denotes denotes the surface over-potential
- \( \psi \) denotes the Helmholtz free energy density
- \( \omega_{a} \) denotes the coefficient of chemical expansion of neutral Lithium in the host material
- \( \Omega \) denotes a domain at the macro scale

1.4 Constants and parameters
- \( N_{A} \) is Avogadro’s number, \( N_{A} = 6.02214129(27) \times 10^{23} \text{mol}^{-1} \)
- \( e \) is elementary charge, \( e = 1.602176565(35) \times 10^{-19} \text{C} \)
- \( F = N_{A} e \) is Faraday’s constant, \( F = 96485.3383 \text{C mol}^{-1} \)
- $R$ is the universal gas constant $8.3144621 \, \text{JK}^{-1}\text{mol}^{-1}$
- $\varepsilon_0$ is the vacuum permittivity or electric constant, $8.85418782 \times 10^{-12} \, \text{F m}^{-1}$

## 2 Introduction

Batteries are by far the most common form of storing energy [1]. Li-ion batteries, particularly the next generation silicon based technology [2], have the potential to span from several megawatt huge battery installations used for "spinning reserves" to ensure grid reliability, to automotive, aerospace, medical, and military industries.

There is being great interest in developing next generation of Li-ion battery for higher capacity and longer life of cycling, in order to develop significantly more demanding energy storage requirements for humanity existing and future inventories of power-generation and energy-management systems [3, 4]. Industry and academic are looking for alternative materials and Silicon is one of the most promising candidates for the active material in anodes, because it has a high theoretical specific energy capacity. At the same time, huge efforts are devoted to cathode materials investigations, as for rechargeable lithium-oxygen or Li-S batteries [5].

Li-ion batteries are based on the classical intercalation reaction during which Li is inserted into or extracted from electrodes [6, 7]. Large volume changes are associated with this process. They induce experimentally observed inelastic effects [8, 9], phase-segregation [10], micro-cracks and particle fracture [11], decrepitation or pulverization, loss of integrity and of electric contact with current collector. This major liability is obstructing the way toward widespread application of the next generation technology and limited the use of lithium batteries to relatively low power applications such as portable devices.

Stress evolution, diffusion, and fracture in representative battery microstructures have been investigated in a long series of recent publications. Most of them are relevant to single particle analysis, nano-wires, or thin films. Some dealt with the multi-scale and multi-physics modeling of the whole battery cell [12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22]. The electrochemical and mechanical performance of Li-ion batteries strongly depends on the interaction between micro and nano-scale phenomena, in particular within the electrodes. Intercalation, swelling and the consequent mechanical failures originate at a scale three order of magnitudes smaller than the battery cell scale, at which ion mobility is usually modeled. Directly resolving all scales and modeling all particles in the electrodes is not practical. Instead, the nano-scale effects are incorporated into the micro-scale problem through homogenization approaches and constitutive models that are derived from homogenization methods. This idea has been pursued by several authors, among others [15, 19, 20], via Mori-Tanaka, Hashin-Strickman, and Wiener bounds. Moving from the state of art of the field, the present contribution aims at tailoring the Computational Homogenization technique [23], using a multiscale scheme with a complex multi-particle representative volume element (RVE).

An electrochemical cell necessarily consists of several phases [24]. They must include two electrode metals, a separator, and an electrolytic solution. An electrode is a material in which electrons are the mobile species. An electrolyte is a material in which the mobile species are ions and free movement of electrons is blocked. Accordingly, mass must be transported through the electrolyte from one electrode to the other to bring reactants to the interfaces, whereas electrons flow in the external conductor and finally travel through the electrodes, doing work or requiring energy. A binary ionic compound is a salt consisting of only two elements in which both elements are ions, a cation (which has a positive charge) and an anion (which has a negative charge). An electrolyte that contains only one solvent and one salt is called a binary electrolyte.

The difference in electric potential between the two electrodes when they are not connected by an external circuit and are in electrochemical equilibrium is called open-circuit potential. When such a potential difference is kept constant during charging, the process is termed potentiostatic. Its dual, when steady battery current is applied, is termed galvanostatic.

Mass transfer in an electrolytic solution requires a description of the movement of mobile ionic species. In the absence of convection, as assumed henceforth, movement of species is governed by diffusion, driven by gradients of concentration, and by migration due to an electric field for the species that are charged. In addition to a standard balance for the species concentration, the virtual-power approach [25] is used to develop the other balances in the formulation.
In section 5 a rigorous thermodynamic analysis is performed, to provide a set of thermodynamic restrictions that shall be satisfied by constitutive specifications. Besides framing the theory in a rigorous setting, thermodynamics provides a firm basis for the multi scale homogenization scheme developed in section 7. The micro to macro scale transition which stems from the so-called Hill-Mandel condition, moves from the energy and entropy balances developed in section 5 in view of the potential-based formulation here adopted.

In order to focus on the novelties of the two-scale formulation, some simple hypothesis will be made throughout the paper. The battery cell is supposed to have a single binary electrolyte which is a solution of a binary salt, say LiX, plus solvent, say a polymer, in which the concentrations of ionic species vary with location in the cell. Active particles in the composite electrodes are idealized as network solids following Larche and Cahn [26], with the lattice material assumed as insoluble in the electrolyte. The concentration of ions in the solid phases is neglected. Magnetic fields and polarization are neglected as well.

There are no reasons to restrict ourselves to simple elastic materials and small displacements and strains apart from simplicity. Whereas small deformations is still an adopted hypothesis in simulations (see for instance [22]), extension to general kinematics and dissipative materials may be carried out following [18, 27]. Special care must be taken however to the proper configuration - either current or reference - in which the scale transitions shall be formulated (see for instance [28, 29]) for a broader discussion on the matter). To avoid adding technical complexities that may further involve the already complicated scenario here depicted, small displacements and strains have been taken.

The computational homogenization technique is essentially based on the solution of nested boundary value problems, one for each scale. A complete set of equations and boundary conditions governing the stress, electric, chemical, and electrochemical potentials (eventually the concentration field as well) are derived for the whole battery cell for both scales in sections 7.1, 7.2 following nonequilibrium thermodynamics of porous electrodes [24, 20]. Two macroscopic phases (solid and electrolyte) and three phases at the micro scale (electrolyte, active particles, conductive particles) are modeled. The binder has not been taken into account in the RVE. At the micro-scale, the ionic fluxes in all phases are related to electrochemical potential gradients, consistent with non-equilibrium thermodynamics. Intercalation kinetics, expressed by Butler-Volmer equations, model the flux of Lithium between the particles and the electrolyte, which at the macro scale is modeled as a bulk supply. At such a scale, transport and stress evolution are modeled via volume averaged conservation equations.

The solution of nested boundary value problems can be only approximated numerically. This task is not attempted here, yet discretized weak forms and the Newton-Raphson procedure are provided in section 8. The numerical solution is typically achieved with two nested finite element simulations (whence the acronym FE²) but in principle there is no reason to exclude other numerical techniques. The implementation and the consequent numerical solution will be the subject of forthcoming publications.

### 3 Local balance laws for diffusing species

#### 3.1 Mass balance

The mass balance equation may be written as

\[ \frac{\partial c_\alpha}{\partial t} + \text{div} [h_\alpha] = h_\alpha \]  

where: \( c_\alpha \) is the molarity (i.e. the number of moles per unit volume) of a generic species \( \alpha \); \( h_\alpha \) is the mass flux in terms of moles, i.e. the number of moles of species \( \alpha \) measured per unit area per unit time; \( h_\alpha \) is the mass supply in terms of moles, i.e. the number of moles of species \( \alpha \) measured per unit volume per unit time. It applies to ions Li\(^+\), X\(^-\), electrons e\(^-\), as well as neutral Li.

#### 3.2 Gauss law

Gauss’s law relates the distribution of electric charge \( \zeta \) (in Coulombs per unit volume) to the resulting electric field \( \mathbf{E} \) (in Volts per meter).

\[ \text{div} [\mathbf{E}] = \frac{1}{\varepsilon_0} \zeta \]
The factor $\varepsilon_0$ is termed vacuum permittivity or electric constant. Its value is $8.85418782 \times 10^{-12} \, \frac{C}{Vm}$.

### 3.3 Faraday’s law

In a solution charge is transported by ions and the flux of mass of each species contributes to a current density in view of Faraday’s Laws of Electrolysis

$$i = F \sum \alpha z_\alpha h_\alpha, \quad i = F \sum \alpha z_\alpha h_\alpha$$

where $F = 96485.3383 \, \text{C mol}^{-1}$ is Faraday’s constant and $z_\alpha$ is the valency$^1$ of ion $\alpha$. The continuity law in terms of charge density $\zeta$, electric current density $i$ (in Amperes per unit area) and charge supply $i$ (in Coulombs per unit volume per unit time) reads

$$\frac{\partial \zeta}{\partial t} + \text{div} \{ i \} = i$$


As in [27] the fundamental assumption will be made that the power expended by each “rate-like” kinematical descriptor can be expressed in terms of an associated force system consistent with its own balance. In the simplistic assumption of small displacements and strains, the conjugated pairs within the internal expenditure of virtual power $W_{\text{int}}$ are the Cauchy stress $\sigma$ and the small strain tensor $\varepsilon$, whose hatted amount $\hat{\varepsilon}$ is taken here as a virtual velocity field. The principle of virtual power (with the two requirements: Power balance $W_{\text{ext}} = W_{\text{int}}$ on any part, frame indifference for $W_{\text{int}}$ on any part for any virtual velocity) leads to the usual balance of forces:

$$\text{div} \{ \sigma \} + b = 0$$

and to the symmetry of tensor $\sigma$. Among bulk forces $b$ the electrostatic forces of interaction of a charge density $\zeta$ in an electric field $E$ will be denoted by $b_\zeta = \zeta E$. Balance equation (5) states that electric and stress fields are unavoidably related in the presence of charge densities and such a relationship has not a constitutive nature. Electroneutrality assumption, see appendix 0, uncouples the fields in the balance equation.

In homogenization theory, it is generally assumed that the internal expenditure of virtual power $W_{\text{int}}$ is preserved in the scale transition:

$$W_{\text{int}}^M = W_{\text{int}}^m$$

with apexes $M$ and $m$ denoting macro and micro scale, respectively. Such a condition is usually known as Hill-Mandel condition [30]. In the present work, assumption (6) will be extended, so that the internal expenditure of virtual power of mechanical forces, of charge and mass fluxes is preserved in the scale transition - see section 7.3.4.

### 5 Thermodynamics

#### 5.1 Energy balance

As usual in continuum mechanics, one can write the local form of the first principle in terms of rates of the specific internal energy $u$:

$$\rho \dot{u} = \sigma \cdot \dot{\varepsilon} + q - \text{div} \{ q \} + \sum \alpha \mu_\alpha h_\alpha - \text{div} \{ \mu_\alpha h_\alpha \}$$

One recognizes three contributions in the variation of internal energy: a mechanical contribution $\sigma \cdot \dot{\varepsilon}$ in which $\varepsilon$ is the small strain tensor and $\sigma$ the Cauchy stress tensor; a heat flux contribution $q - \text{div} \{ q \}$ where

\[ ^1 \text{i.e. the number of electrons transferred per ion, typically } +1 \text{ for Li}^+ \text{ cations and } -1 \text{ for X}^- \text{ anions.} \]
the scalar \( q \) is the heat supplied by external agencies and \( \mathbf{q} \) is the heat flux vector; a mass flux contribution \( \rho \dot{\mathbf{h}} = \text{div} [\mathbf{P} \mathbf{h}] \) with the scalar \( \mathbf{P} \) denoting the electrochemical potential, the scalar \( h \) the species supply\(^2\) and \( \mathbf{h} \) the mass flux vector. Mass flux and supply refer to electrons, to neutral and ionic species and it is here left unsaid that \( \alpha \) ranges from 1 to the total number of species.

In the electrodes, charge flux is due to electrons by definition. Lithium intercalation is neutral and takes place in active particles merely. In view of the hypothesis made, the energy balance in the active particles reads:

\[
\rho \dot{u} = \sigma \cdot \dot{\varepsilon} + q - \text{div} [\mathbf{q}] + \mu \text{Li} \cdot \text{div} [\mu \text{Li} \cdot \mathbf{h}] + \text{div} [\mu e^- \cdot h e^- - \text{div} [\mu e^- \cdot h e^-]]
\]  

(8)

In conductive particles and in the binder within electrodes no intercalation takes place. Balance equation (7) becomes

\[
\rho \dot{u} = \sigma \cdot \dot{\varepsilon} + q - \text{div} [\mathbf{q}] + \text{div} [\mu e^- \cdot h e^- - \text{div} [\mu e^- \cdot h e^-]]
\]  

(9)

In the electrolyte charge is transported by ions and the flux of mass of each species contributes to a current density in view of Faraday’s Laws of Electrolysis,

\[
\rho \dot{u} = \sigma \cdot \dot{\varepsilon} + q - \text{div} [\mathbf{q}] + \sum_\alpha \mu \alpha \rho_\alpha \cdot \hat{\mathbf{h}}_\alpha - \text{div} [\mu \alpha \cdot \hat{\mathbf{h}}_\alpha]
\]  

(10)

5.2 Entropy imbalance

The entropy imbalance can be given a local form in terms of the specific entropy \( \eta \) and of the absolute temperature \( \theta \):

\[
\rho \dot{\eta} - \dot{\mathbf{q}} \cdot \theta + \text{div} \left[ \frac{\mathbf{q}}{\theta} \right] \geq 0
\]  

(11)

By noting that \( \text{div} \left[ \frac{\mathbf{q}}{\theta} \right] = \frac{1}{\theta} \text{div} [\mathbf{q}] - \frac{1}{\theta^2} \mathbf{q} \cdot \nabla [\theta] \) the entropy imbalance can be expressed in terms of internal energy:

\[
\rho \dot{\eta} - \left\{ \rho \dot{u} - \sigma \cdot \dot{\varepsilon} - \sum_\alpha \mu \alpha \rho_\alpha \cdot \hat{\mathbf{h}}_\alpha - \text{div} [\mu \alpha \cdot \hat{\mathbf{h}}_\alpha] \right\} - \frac{1}{\theta} \mathbf{q} \cdot \nabla [\theta] \geq 0
\]  

(12)

For simple elastic materials one may consider the internal energy to be function of the entropy \( \eta \), of kinematic variables here represented by the small strain tensor \( \varepsilon \), of the concentrations \( c_\alpha \). One has therefore

\[
\dot{u} = \frac{\partial u}{\partial \eta} \dot{\eta} + \frac{\partial u}{\partial \varepsilon} \cdot \dot{\varepsilon} + \sum_\alpha \frac{\partial u}{\partial c_\alpha} \dot{c}_\alpha
\]  

(13)

to be inserted in (12).

For the active particles the entropy imbalance (12) specifies as:

\[
\rho \dot{\eta} - \left\{ \rho \dot{u} - \sigma \cdot \dot{\varepsilon} - (\mu \text{Li} \cdot \text{div} [\mu \text{Li} \cdot \mathbf{h}] - (\mu e^- \cdot h e^+ - \text{div} [\mu e^- \cdot h e^-]) \right\} - \frac{1}{\theta} \mathbf{q} \cdot \nabla [\theta] \geq 0
\]  

(14)

in view of (8). Accounting for mass and charge balances (1-4):

\[
\mu \text{Li} \cdot \text{div} [\mu \text{Li} \cdot \mathbf{h}] = \mu \text{Li} \cdot \dot{\mathbf{c}} \text{Li} - \mathbf{h} \text{Li} \cdot \nabla [\mu \text{Li}] \]  

(15)

\[
\mu e^- \cdot h e^- - \text{div} [\mu e^- \cdot h e^-] = \mu e^- \cdot \dot{\mathbf{c}} e^- - h e^- \cdot \nabla [\mu e^-] \]  

(16)

it finally becomes

\[
\rho \dot{\eta} \left( \theta - \frac{\partial u}{\partial \eta} \right) + \dot{\varepsilon} \cdot (\sigma - \rho \frac{\partial u}{\partial \varepsilon}) + \dot{c} \text{Li} \left( \mu \text{Li} - \rho \frac{\partial u}{\partial \text{cLi}} \right) + \dot{c} e^- \left( \mu e^- - \rho \frac{\partial u}{\partial \text{ce}^-} \right) + \mathbf{h} \text{Li} \cdot \nabla [\mu \text{Li}] - \mathbf{h} e^- \cdot \nabla [\mu e^-] - \frac{1}{\theta} \mathbf{q} \cdot \nabla [\theta] \geq 0
\]  

(17)

By applying the Coleman-Noll procedure above, one requires that the latter inequality must be satisfied for all constitutive processes [31, 32]. This leads to the following thermodynamic restrictions:

\[
\dot{\theta} - \frac{\partial u}{\partial \eta} = 0, \quad \sigma - \rho \frac{\partial u}{\partial \varepsilon} = 0, \quad \mu \text{Li} - \rho \frac{\partial u}{\partial \text{cLi}} = 0, \quad \mu e^- - \rho \frac{\partial u}{\partial \text{ce}^-} = 0,
\]

\(^2\)Typically by intercalation
h_{Li} \cdot \nabla [\mu_{Li}] \leq 0, \quad h_{e^-} \cdot \nabla [\pi_{e^-}] \leq 0, \quad \frac{1}{\vartheta} q \cdot \nabla [\vartheta] \leq 0 \quad (18)
onumber

on any active particle.

Following the same path of reasoning for the conductive particles, where no ionic mass transport takes place, the entropy imbalance (14) is obtained in the form

\[ \rho \dot{\eta} \left( \vartheta - \frac{\partial u}{\partial \eta} \right) + \dot{\varepsilon} \cdot \left( \sigma - \rho \frac{\partial u}{\partial \varepsilon} \right) + c_{e^-} \left( \pi_{e^-} - \rho \frac{\partial u}{\partial c_{e^-}} \right) - h_{e^-} \cdot \nabla [\pi_{e^-}] - \frac{1}{\vartheta} q \cdot \nabla [\vartheta] \geq 0 \quad (19) \]

whence the thermodynamic restrictions:

\[ \vartheta - \frac{\partial u}{\partial \eta} = 0, \quad \sigma - \rho \frac{\partial u}{\partial \varepsilon} = 0, \quad \pi_{e^-} - \rho \frac{\partial u}{\partial c_{e^-}} = 0, \]

\[ h_{e^-} \cdot \nabla [\pi_{e^-}] \leq 0, \quad \frac{1}{\vartheta} q \cdot \nabla [\vartheta] \leq 0 \quad (20) \]

In the electrolyte, in view of the balance of energy (10), the entropy imbalance can be written as

\[ \rho \dot{\eta} - \left\{ \rho \dot{u} - \sigma \cdot \dot{\varepsilon} - \sum_{\alpha} \pi_{\alpha} h_{\alpha} - \text{div} [\pi_{\alpha} h_{\alpha}] \right\} - \frac{1}{\vartheta} q \cdot \nabla [\vartheta] \geq 0 \quad (21) \]

which, in view of (13) turns out to

\[ \rho \dot{\eta} \left( \vartheta - \frac{\partial u}{\partial \eta} \right) + \dot{\varepsilon} \cdot \left( \sigma - \rho \frac{\partial u}{\partial \varepsilon} \right) + \sum_{\alpha} \left( \pi_{\alpha} h_{\alpha} - \text{div} [\pi_{\alpha} h_{\alpha}] - \rho \frac{\partial u}{\partial c_{\alpha}} \dot{c}_{\alpha} \right) - \frac{1}{\vartheta} q \cdot \nabla [\vartheta] \geq 0 \]

as no electron flux takes place in the electrolyte, \( \dot{c}_{e^-} = 0 \). Accounting for mass balance (1)

\[ \pi_{\alpha} h_{\alpha} - \text{div} [\pi_{\alpha} h_{\alpha}] = \pi_{\alpha} \dot{c}_{\alpha} - h_{\alpha} \cdot \nabla [\pi_{\alpha}] \quad (22) \]

the entropy imbalance finally becomes

\[ \rho \dot{\eta} \left( \vartheta - \frac{\partial u}{\partial \eta} \right) + \dot{\varepsilon} \cdot \left( \sigma - \rho \frac{\partial u}{\partial \varepsilon} \right) + \sum_{\alpha} \dot{c}_{\alpha} \left( \pi_{\alpha} - \rho \frac{\partial u}{\partial c_{\alpha}} \right) - \sum_{\alpha} h_{\alpha} \cdot \nabla [\pi_{\alpha}] - \frac{1}{\vartheta} q \cdot \nabla [\vartheta] \geq 0 \quad (23) \]

and the thermodynamic restrictions

\[ \vartheta - \frac{\partial u}{\partial \eta} = 0, \quad \sigma - \rho \frac{\partial u}{\partial \varepsilon} = 0, \quad \pi_{\alpha} - \rho \frac{\partial u}{\partial c_{\alpha}} = 0, \]

\[ \sum_{\alpha=1}^{2} h_{\alpha} \cdot \nabla [\pi_{\alpha}] \leq 0, \quad \frac{1}{\vartheta} q \cdot \nabla [\vartheta] \leq 0 \quad (24) \]

come out for all \( \alpha \).

5.2.1 Remarks

According to Hatsopoulos and Gyftopoulos, [33] section 7.6, an important feature of electrostatic field \( E \) is that the net electric charge \( \zeta \) is independent on the electrostatic potential \( \phi \). Therefore, the energy of the system can be written as a sum of two terms, one representing the energy in the absence of the force field and the other representing the energy due to force field. Accordingly,

\[ \rho \dot{\varepsilon} = \rho \dot{u} + \text{div} \left[ \phi \mathbf{E} \right] - \frac{1}{\varepsilon_0} \zeta \dot{\phi} \]

In view of Gauss’ law (2), and denoting with \( \tau = \nabla [\phi] \) it comes out:

\[ \rho \dot{\varepsilon} = \rho \dot{u} + \mathbf{E} \cdot \dot{\tau} \quad (25) \]

7
If the total energy $e(\eta, \varepsilon, c_\alpha, \phi)$ is assumed to be dependent on $\phi$ in terms of $\tau$ only, one has

$$\dot{e} = \dot{u} + \frac{\partial e}{\partial \tau} \cdot \dot{\tau}$$

(26)

Accordingly, entropy imbalances (17), (19), and (23) contain a further term

$$\dot{\tau} \cdot \left( E - \rho \frac{\partial e}{\partial \tau} \right)$$

(27)

which vanishes after applying the Coleman-Noll procedure. Thermodynamic restriction

$$E - \rho \frac{\partial e}{\partial \tau} = 0$$

(28)

corresponds. This approach - with the modification of considering the nominal electric displacement rather than the electric field because of the electric dipole moments in the material - is also customary in dielectric materials, see among others [34].

Different thermodynamic potentials can be considered rather than the internal energy $u$. A classical one is the Helmholtz free energy $\psi(\vartheta, \varepsilon, c_\alpha, \phi) = e(\eta, \varepsilon, c_\alpha, \phi) - \vartheta \eta$. The Grand or Landau potential $\Phi$ for simple elastic materials it is a function of the temperature $\vartheta$, of kinematic variables $\varepsilon$, of the electrochemical potentials $\mu_\alpha$ and of the electric potential $\phi$. It is related to the specific energy $e$ by the Legendre transform:

$$\Phi(\vartheta, \varepsilon, \mu_\alpha, \phi) = e(\eta, \varepsilon, c_\alpha, \phi) - \vartheta \eta - \sum_\alpha \rho^{-1} c_\alpha \mu_\alpha$$

(29)

It is straightforward to show that the following thermodynamic restriction applies:

$$c_\alpha + \rho \frac{\partial \Phi}{\partial \mu_\alpha} = 0$$

(30)

By the Legendre transform

$$r(\eta, \varepsilon, c_\alpha, E) = e(\eta, \varepsilon, c_\alpha, \phi) - \rho^{-1} \tau \cdot E$$

(31)

the new thermodynamic restriction

$$\tau + \rho \frac{\partial r}{\partial E} = 0$$

(32)

descends.

6 Electrode kinetics

Lithium deposition or dissolution

$$\text{Li} \rightleftharpoons \text{Li}^+ + e^-$$

(33)

cannot be treated as a simple chemical reaction in a single phase since the process must generate or consume electrical charge, and this will always be accompanied by the formation of an electrostatic potential difference between the two phases. If the chemical potential $\mu_{\text{Li}}$ exceeds the electrochemical potential of the Lithium ions in the solution $\mu_{\text{Li}}$, and electrons in the metal $\mu_e$, then Li dissolution takes place and the solution next to the electrode will become positively charged with respect to the electrode itself. A so-called double layer is set whose modeling is not carried out here. By assuming the double layer as a zero-thickness interface, during charge and discharge a discontinuity in electrical potential $\xi$ arises between an electrode and its surrounding solution which in turn depends on the velocity of the battery operation.

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3 The modeling of the double layer is mainly due to the work of Stern, Gouy and Chapman, see [35] for details.
The potential jump may inhibit further dissolution. The value of the electrical potential discontinuity at the thermodynamic equilibrium for reaction (33) is termed $\xi_{\text{Nernst}}$ and is related to the activity coefficient of Li brought in contact with a solution of its ions. The potential difference

$$\chi = \xi - \xi_{\text{Nernst}}$$

is called surface over-potential. A net current passing between electrode and solution is related to $\chi$.

As stated above, the departure from thermodynamic equilibrium is due to the imbalance of electrochemical potentials in reaction (33), which is the driving force for the electrode reaction. Imbalance is measured by the amount $\gamma$, defined as

$$\gamma = \mu_{\text{Li}} - \mu_{e^-} - \mu_{\text{Li}^+}$$

and thermodynamic equilibrium is clearly reached if and only if $\gamma = 0$. A relation between $\gamma$ and $\chi$ is constitutive in nature and will be discussed in appendix 0.

The mass flux in the outward normal direction $\mathbf{n}$ at the surface of an electrode is related by Faraday's law to the current density $\mathbf{i} \cdot \mathbf{n}$ in the same direction. The macroscopic relationship between $\mathbf{i} \cdot \mathbf{n}$ and $\chi$ and the composition adjacent to the electrode surface is usually described by means of the Butler-Volmer equation [24, 35]:

$$\mathbf{i} \cdot \mathbf{n} = i_0 \left\{ \exp \left( \frac{(1 - \beta)}{R \vartheta F} F \chi \right) - \exp \left[ -\frac{\beta}{R \vartheta F} F \chi \right] \right\}$$

Factor $i_0$, termed exchange current density, depends generally on the composition of the solution adjacent to the electrode. It is often assumed to be constant at a metallic anode. Parameter $\beta$ is called symmetry factor and represents the fraction of the surface over potential that promotes cathodic reaction. It is widely assumed $\beta = 1/2$. The reader may refer to specialized literature [24, 36] for further details.

As observed in [18], by using the Butler-Volmer equation stress can only influence reaction by means of the electrochemical potentials, i.e. by altering the concentrations of the reacting species, because mechanic fields does not enter equation (36) directly. A more refined model of the interaction of mechanics and electrochemical reactions involve the mechanical characterization of the Stern and Gouey-Chapman layers, the former of which has atomistic size. Such an attempt is not carried out in the present note, the reader may refer to [18, 35].

7 Multiscale formulation.

A schematization of a Li-Ion battery is shown in Figure 1 for a half-cell with a metallic Lithium electrode (Figure 1-a) as well as for a whole cell with porous electrodes (Figure 1-b). The behavior of the battery cell is intrinsically multi-scale, as the multi-physics phenomena involving diffusion, migration, intercalation, and their mechanical effects take place at the length scale proper of the electrode compound. A numerical simulation must incorporate these effects. Unfortunately, discretizing the whole battery cell at the particle characteristic size is currently computationally unfeasible. Recourse is thus made to homogenization schemes. Golmon et. al [15, 19] considered the Mori-Tanaka approach at a meso-scale; Hashin-Strickman as well as Wiener bounds have been considered by Ferguson et al [20]. In this paper the computational homogenization framework [37, 38, 39, 40, 41, 42] is pursued. Computational homogenization is essentially based on the solution of nested boundary value problems, one for each scale. A first order theory is adopted for both the mechanical and electrochemical homogenization procedure which hinges on the principles of local action and of scales separation [43]. Deformation localizations are excluded.

Two scales will be considered to model composite electrodes and porous separators $\Omega_P = \{\Omega_{\text{An}} \cup \Omega_S \cup \Omega_{\text{Ca}}\}$ - see Figure 1 for notation, whereas a single macroscopic scale is adequate to model the metallic electrodes, the current collectors, as well as all other parts that are homogeneous.

The macroscopic scale modeling is framed into porous materials theory, taking into account the pore-filling electrolyte (from now on with apex e) and the porous solid material (apex E). At the microscopic

---

4The electrolyte in the current technology of Li-ion batteries [7] might be a solid, a liquid or a gel. An up to date discussion on the subject can be found in [44].
level, the electrode is separated into its particles compound (active particles, conducting particles, binder): the representative volume element (RVE) contains them all and the pore-filling electrolyte, as in Figure 2.

At the macroscopic scale, the intercalation of Lithium into the particle is described by a volume supply $h_{Li}$ and no mechanical coupling is provided explicitly. The amount of the intercalated Lithium $h_{Li}$ is not given, as unknown are the constitutive laws for all phenomena involved (diffusion, migration, intercalation, and the mechanical coupling). Those quantities are upscaled from the underlying microstructure.

At the micro-scale all fundamental mechanisms and their coupling are modeled in full. Scale transitions are invoked to: i) allow the solution of the micro scale BVP (the macro to micro scale transition - see section 7.3.1 - that provides boundary condition at the micro scale) by linking it to the set of macroscopic variables that drive the whole problem; ii) provide tangent matrices and updated values of the (dual) macroscopic fields (the micro to macro scale transition - see section 7.3.4), namely the average stress field, ionic mass fluxes, electron current density, concentration of ions in the electrolyte and of Lithium in the electrode, intercalation
supply of neutral Lithium in the electrode. In order to upscale all these quantities, the Hill-Mandel condition and the mass conservation across the scales will be imposed.

7.1 Macroscale

At each point \( x \in \Omega_P \) two continuous phases superpose as for saturated soils. The electrolyte (subscript \( e \)) fills the pores of the electrodes compound and of the separator. Electrodes compound include the active material, binders and conductive additives (subscript \( E \)). The separator includes the solid phase (again subscript \( E \)). Superscript \( M \) distinguishes the macroscopic amounts form the same ones at the micro scale.

For the sake of shortness, a composite cathode \( \Omega_{Ca} \) only will be described in full. The formulation for anodes and separator can be derived straightforwardly. The porosity \( \epsilon_e \) of the electrode is defined as the fraction of void space in the material, where the voids are filled by the electrolyte. It is defined by the ratio:

\[
\epsilon_e = \frac{V_V}{V_T}
\]

where \( V_V \) is the volume of void-space and \( V_T \) is the total volume of material, including the solid and void components. The complementary ratio is denoted by \( \epsilon_E = 1 - \epsilon_e \). Both porosities will be related to the RVE at the micro scale in section 7.2.

7.1.1 Balance equations

The macroscopic mass balance equations characterize the species transport in the phases of composite cathodes, namely: i) the transport of neutral Lithium in the active particles, macroscopically undistinguished from the other particles in the porous electrode; ii) the transport of \( \text{Li}^+ \) cations and \( X^- \) anions in the electrolyte. 

\[
\frac{\partial c^{M_{\text{Li}}} }{\partial t} + \text{div } [ h^{M_{\text{Li}}} ] = h_{\text{Li}} \quad x \in \Omega_{Ca} \times [0,T]
\]

\[
\frac{\partial c^{M_{\text{Li}+}} }{\partial t} + \text{div } [ h^{M_{\text{Li}+}} ] = h_{\text{Li}+} \quad x \in \Omega_{Ca} \times [0,T]
\]

\[
\frac{\partial c^{M_{X^-}} }{\partial t} + \text{div } [ h^{M_{X^-}} ] = 0 \quad x \in \Omega_{Ca} \times [0,T]
\]

The supply \( h_{\text{Li}} \) denotes the average amount at \( x \in \Omega_{Ca} \) of neutral Lithium that intercalates in the active particles, leaving the electrolyte because of chemical reactions at the particle/electrolyte interface. In view of the two scale formulation, \( h_{\text{Li}} \) will be estimated by a scale transition in the homogenization framework - see section 7.3.4; in any case, stoichiometry of the chemical reaction (33) requires

\[
\epsilon_e h_{\text{Li}+} = -\epsilon_E h_{\text{Li}}
\]

in equation (38). The concentrations, the mass flux of species \( h^{M}_a \), and of neutral Lithium \( h^{M}_{\text{Li}} \) will be upscaled within the homogenization procedure.

The flux of charge in the electrode is caused by the transport of electrons \( h^{M}_{e-} \) in the active and conductive particles. For each ion that leaves the electrolyte an electron corresponds that leaves the flux \( h_{e-} = -h_{\text{Li}} \). The balance of charges thus reads:

\[
-F \frac{\partial c^{M_{e-}} }{\partial t} + \text{div } [ i^{M_{e-}} ] = -F h_{e-} \quad x \in \Omega_{Ca} \times [0,T]
\]

Hypothesis has been made that in the active and conductive particles the positively charged cores are steady, i.e. \( h^{M}_{+} = 0 \). According the (given) initial concentration \( c^{M}_{+} \) is maintained during the whole process.

Two separated electric fields are considered at each point, one pertaining to the electrolyte \( E^{M}_{e} \) and one to the electrode \( E^{M}_{E} \). Gauss law is imposed in both phases.

\[
\text{div } [ E^{M}_{E} ] = \frac{F}{\epsilon_0} (c^{M}_{+} - c^{M}_{e-}) \quad x \in \Omega_{Ca} \times [0,T]
\]

\[
\text{div } [ E^{M}_{e} ] = \frac{F}{\epsilon_0} (c^{M}_{\text{Li}+} - c^{M}_{X^-}) \quad x \in \Omega_{Ca} \times [0,T]
\]
It is convenient to express Gauss law in an incremental form. By means of the mass balance equations, easy algebra leads from (41) to

$$\text{div} \left[ \hat{E}_e^M \right] = \frac{F}{\varepsilon_0} (h_{\text{Li}^+} - \text{div} \left[ h_{\text{Li}^+}^M \right] + \text{div} \left[ h_{\text{X}^-}^M \right]) \quad x \in \Omega_{Ca} \times [0, T]$$

whence

$$\text{div} \left[ \hat{E}_e^M + \frac{1}{\varepsilon_0} i_e^M \right] = \frac{F}{\varepsilon_0} h_{\text{Li}^+} \quad x \in \Omega_{Ca} \times [0, T]$$

The counterpart in the electrode reads

$$\text{div} \left[ \hat{E}_e^M + \frac{1}{\varepsilon_0} i_e^M \right] = -\frac{F}{\varepsilon_0} h_{\text{e}^-} \quad x \in \Omega_{Ca} \times [0, T]$$

Equilibrium holds as in (5). Bulk forces are here neglected but the electrostatic forces of interaction $b_e = \zeta E$.

$$\text{div} \left[ \sigma_E^M \right] + F(c_e^M - c_e^-) E_e^M = 0 \quad x \in \Omega_{Ca} \times [0, T]$$

$$\text{skw} \left[ \sigma_E^M \right] = 0 \quad x \in \Omega_{Ca} \times [0, T]$$

$$\text{div} \left[ \sigma_e^M \right] + F(c_{\text{Li}^+}^M - c_{\text{X}^-}^M) E_e^M = 0 \quad x \in \Omega_{Ca} \times [0, T]$$

$$\text{skw} \left[ \sigma_e^M \right] = 0 \quad x \in \Omega_{Ca} \times [0, T]$$

### 7.1.2 Boundary and initial conditions

Initial conditions are suitably taken, depending on the process that is simulated - galvanostatic/potentiostatic, charge/discharge. The battery cell is initially undeformed in any case.

At the anode current collector interface $\Gamma_A$ the electric potential is set to zero, according with the selection of the Li-anode as the reference electrode. A Li-metal anode is here assumed, but extension to porous anode is straightforward: it will be sufficient to apply at the anode the path of reasoning that will be here applied to the porous cathode. During a galvanostatic discharge process with steady current density $i = \text{constant}$ in the current collector. In case of potentiostatic process, the open circuit potential $\xi^{\text{Nernst}}$ in equation (34) can be taken as zero if the anode is used as reference electrode.

At interface $\Gamma_{AS}$ three conditions are enforced. Anions cannot leave the separator, therefore $h_{\text{X}^-} \cdot n = 0$ at a generic point $\Omega_S \ni x \rightarrow \Gamma_{AS}$. Moreover, for every electron that leaves the anode, a Li$^+$ ion enters the electrolyte: thus $F \epsilon_e h_{\text{Li}^+} \cdot n = -I$ at point $\Omega_S \ni x \rightarrow \Gamma_{AS}$. Here the normal is outward with respect to the separator, coherently with the choice of $\Omega_S \ni x$. Finally, a boundary condition of an influx of Li$^+$ ions in the outward normal direction $n$ on the surface $\Gamma_{AS}$ to $\chi$;

$$F \epsilon_e h_{\text{Li}^+} \cdot n = i_0 \left\{ \exp \left[ \frac{(1 - \beta)F}{R \theta} \chi \right] - \exp \left[ -\frac{\beta F}{R \theta} \chi \right] \right\}$$

The open circuit potential $\xi^{\text{Nernst}}$ in equation (48) can be taken as zero if the anode is used as reference electrode.

At interface $\Gamma_{SC}$ continuity conditions for electric potential and electrochemical potentials are imposed because anions and cations are free to pass from the separator to the electrolyte in the porous cathode in a thermodynamic equilibrium condition at the micro scale. Electrons and neutral Lithium cannot exit the cathode, therefore $i_{\text{Li}} = 0$ as well as $h_{\text{Li}} \cdot n = 0$ at $\Omega_{Ca} \ni x \rightarrow \Gamma_{SC}$.

At the cathode-current collector interface $\Gamma_{CC}$, neither Lithium ions, nor counterions, nor neutral Lithium can leave the battery $h_{\text{Li}^+} \cdot n = h_{\text{X}^-} \cdot n = h_{\text{Li}} \cdot n = 0$ at $\Omega_{Ca} \ni x \rightarrow \Gamma_{CC}$. The electrode carries the current $i_F = I$. Such a current is constant in the current collector. In case of potentiostatic process, the electric potential at the current collector boundary $\Gamma_{CC}$ is given.

Mechanical boundary conditions consider no displacements at both ends or an external pressure applied at the boundaries $\Gamma_A$ and $\Gamma_{CC}$.

---

\(^5\)Such a condition is expected at the micro scale only. This is correct for porous materials. However, as the anode foil is here described as homogeneous, the Butler-Volmer interface condition is expressed macroscopically, too.
7.1.3 Weak form

The weak form for the macroscale balance equations and boundary conditions\(^6\) can be given in terms of the potentials, displacements, and concentrations in a time interval \([0,T]\) as

\[
\frac{d}{dt} b\left(\mathbf{z}^M(t), \tilde{y}^M\right) + a\left(\mathbf{y}^M(t), \tilde{y}^M\right) = f\left(\tilde{y}^M\right) \quad \forall \tilde{y}^M \in \mathcal{V}
\]

The identification of the functional spaces \(\mathcal{V}[0,T]\), \(\mathcal{V}\) falls beyond the scope of the present note. The former space includes time dependent functions, whereas space \(\mathcal{V}\) does not (see [45], chapter 12). Vectors \(\mathbf{z}^M\) and \(\mathbf{y}^M\) collect the time-dependent unknown fields. The former contains the concentration fields

\[
\mathbf{z}^M = \{\epsilon_{Li}^M, \epsilon_{Li}^e, \epsilon_{Li}^{M+}, \epsilon_{X}^{M-}\}
\]

whereas the latter contains all the potentials and displacements

\[
\mathbf{y}^M = \{\mu_{Li}, \mu_{e}, \mu_{Li}^+, \mu_{X}^-, \phi_{e}^M, \phi_{Li}^M, u^M\}
\]

Vector \(\tilde{y}^M\) collects the steady-state test functions that correspond to the unknown fields in \(\mathbf{y}^M\). Vector \(\mathbf{z}^M\) should be dependent on \(\mathbf{y}^M\) by some constitutive equations, as the ones derived from the Landau potential (30). It is well known that in the computational homogenization technique such a constitutive dependency is imposed only incrementally, with tangent modulus upscaled from the micro scale. Bilinear forms \(a(\cdot,\cdot)\) and \(b(\cdot,\cdot)\) are defined as

\[
b\left(\tilde{y}^M, \mathbf{z}^M\right) = -\int_{\Omega_{Ca}} \epsilon_E \left(\tilde{\mu}_{Li}^M \epsilon_{Li}^M + \tilde{\mu}_e^M \epsilon_{Li}^e\right) + \epsilon_E \left(\tilde{\mu}_{Li}^+ \epsilon_{Li}^{M+} + \tilde{\mu}_{X}^- \epsilon_{X}^{-}\right) \, d\Omega
\]

\[
a\left(\tilde{y}^M, \mathbf{y}^M\right) = \int_{\Omega_{Ca}} \epsilon_E \left(\nabla \left[\tilde{\mu}_{Li}^M \right] \cdot \mathbf{h}_{Li}^M + \nabla \left[\tilde{\mu}_e^M \right] \cdot \mathbf{h}_e^M\right) + \epsilon_E \left(\nabla \left[\tilde{\mu}_{Li}^+ \right] \cdot \mathbf{h}_{Li}^{M+} + \nabla \left[\tilde{\mu}_{X}^- \right] \cdot \mathbf{h}_X^{-}\right) \, d\Omega
\]

\[
+ \int_{\Omega_{Ca}} \epsilon_E \left\{\nabla \left[\tilde{\phi}_e^M \right] \cdot \left(\tilde{E}_e^M + \frac{1}{\epsilon_0} \mathbf{1}_e^M\right)\right\} + \epsilon_E \left\{\nabla \left[\tilde{\phi}_{Li}^M \right] \cdot \left(\tilde{E}_{Li}^M + \frac{1}{\epsilon_0} \mathbf{1}_{Li}^M\right)\right\} \, d\Omega
\]

\[
+ \int_{\Omega_{Ca}} \sigma^M \cdot \tilde{\xi}^M + \epsilon_E F \epsilon_{e}^M \mathbf{E}_e^M \cdot \tilde{\mathbf{u}}^M - \epsilon_e F (\epsilon_{Li}^{M+} - \epsilon_{X}^{-}) \mathbf{E}_{Li}^M \cdot \tilde{\mathbf{u}}^M \, d\Omega
\]

\[
+ \int_{\Omega_{Ca}} \tilde{h}_{Li} \left(\tilde{\gamma}^M + \frac{F}{\epsilon_0} \tilde{\xi}^M\right) \, d\Omega
\]

with \(\tilde{h}_{Li} = \epsilon_E h_{Li} = \epsilon_E h_{Li}^- = -\epsilon_e h_{Li}^{M+}, \tilde{\gamma}^M = \tilde{\mu}_{Li}^M - \tilde{\mu}_e^M - \tilde{\mu}_{Li}^+ + \tilde{\mu}_{X}^-\), and \(\tilde{\xi}^M = \tilde{\phi}_e^M - \tilde{\phi}_{Li}^M\). The given terms are due to the electrostatic interactions in the bulk and to the eventual tractions on the Neumann part of the boundary of the electrode \(\partial \Omega_{Ca}\).

\[
f(\tilde{y}^M) = \int_{\Omega_{Ca}} \epsilon_E F c_{e}^M \mathbf{E}_e^M \cdot \tilde{\mathbf{u}}^M \, d\Omega + \int_{\partial \Omega_{Ca}} \mathbf{T} \cdot \tilde{\mathbf{u}}^M \, d\Gamma
\]

The weak form here proposed is remarkably different from other forms in the literature [15, 19, 22] for being written in terms of electrochemical potentials rather than concentrations. By this choice the weak form maintains the usual physical meaning of power expenditure, what is here mandatory to perform the correct scale transitions. A similar path of reasoning has been recently followed for the problem of hydrogen embrittlement [46], that indeed shows several similarities with the one at hand. As an eventual drawback, this formulation might make the numerical solution more involved. Such an eventuality was not pointed out in [46], at any rate.

7.2 Microscale

The evolution of electrochemical and mechanical fields at the finest scale is defined and monitored on an RVE of volume \(V\) and boundary \(\partial \Omega\). It is provided with the essential physical and geometrical information

As no constitutive laws are assumed at the macro-scale the notion of governing equations is vacuous at such a scale.
about the microstructural components, that are the active particles, the binder, the conductive particles, and the pore filling electrolyte. The choice of the RVE is a delicate task, as the RVE should be statistically representative of all microstructural particles and phenomena, and at the same time should remain small enough so that the principle of scale separation is not violated. Theoretically, the principle of scale separation assumes an infinitesimally small underlying fine scale structure (infinitesimal neighborhood of a material point) though finite sized RVEs are used in real predictive computations.

Two kinds of particles are modeled within the RVE. The active particles (collectively occupying domain $V_a$) and the conductive particles that define domain $V_c$. The binder, that could be modeled as a cohesive interface between particles, currently has not been considered. Accordingly, the solid phase will occupy volume $V_E = V_a \cup V_c$. The electrolyte will fill all the remaining parts of the RVE, in domain $V_e$ such that $V = V_E \cup V_e$.

### 7.2.1 Balance equations

The microscopic mass balance equations characterize the species transport in two phases, namely the transport of neutral Lithium in the active particles and the transport of $\text{Li}^+$ and $X^-$ ions in the electrolyte.

\[
\frac{\partial c_{\text{Li}}^m}{\partial t} + \text{div} \left( h_{\text{Li}}^m \right) = 0 \quad x \in V_a \tag{53}
\]

\[
\frac{\partial c_{\text{Li}}^m}{\partial t} + \text{div} \left[ h_{\text{Li}}^m \right] = 0 \quad x \in V_c \tag{54}
\]

\[
\frac{\partial c_{X}^m}{\partial t} + \text{div} \left[ h_{X}^m \right] = 0 \quad x \in V_e \tag{55}
\]

There is no supply of species at the micro scale, as intercalation phenomena are analytically described along interfaces without any homogenization assumption. Current density in active and conductive particles is due to electron transport, and the local form of mass and charge conservation read:

\[
\frac{\partial c_{e}^m}{\partial t} + \text{div} \left[ h_{e}^m \right] = -\frac{1}{F} \left( \frac{\partial c_{e}^m}{\partial t} + \text{div} \left[ i_{e}^m \right] \right) = 0 \quad x \in V_E \tag{56}
\]

Charge and mass equations for electrons are equivalent in the assumption that the positively charged cores are steady.

Gauss law governs the electric field $E^m$.

\[
\text{div} \left[ E^m \right] = \frac{F}{\varepsilon_0} \left( c_{e}^m - c_{e}^m \right) \quad x \in V_E \tag{57}
\]

\[
\text{div} \left[ E^m \right] = \frac{F}{\varepsilon_0} \left( c_{\text{Li}^+}^m - c_{X^-}^m \right) \quad x \in V_e \tag{58}
\]

Incrementally, they hold

\[
\text{div} \left[ E^m_e + \frac{1}{\varepsilon_0} i_{e}^m \right] = 0 \quad x \in V_e \tag{59}
\]
\[
\text{div} \left[ \frac{1}{\varepsilon_0} \mathbf{1}_m \right] = 0 \quad \mathbf{x} \in V_E
\] (60)

Inertia effects as well as non electrostatic bulk forces are neglected, so that the force balance (5) specializes as:

\[
\text{div} \left[ \sigma^m \right] + F(c^m_m - c^m_{X^-}) \mathbf{E}^m = \mathbf{0} \quad \mathbf{x} \in V_E
\] (61)

\[
\text{div} \left[ \sigma^m \right] + F(c^m_{Li^+} - c^m_X^-) \mathbf{E}^m = \mathbf{0} \quad \mathbf{x} \in V_e
\] (62)

skw[\sigma^m] = 0 \quad \mathbf{x} \in V (63)

7.2.2 Interface conditions

7.2.2 Interface conditions

In the present multiscale framework, continuity of displacements and surface tractions are imposed at all interfaces. This hypothesis is indeed strong and implies essentially that the binder is modeled as a perfect adhesive with zero thickness. A cohesive interface model would definitely be more adequate but such a formulation, which overall does not make the problem much more involved, is useless until material parameters are measured, especially in terms of capability of transferring mass and charge against a critical detachment of particles. Such a crucial aspect is related to the failure mode of electrodes, topic that goes beyond the scope of the present work and will constitute subject of further developments.

To the sake of clearness, it will be denoted with:

\[
\pi |_{w} = \pi (\mathbf{x}) \quad V_w \ni \mathbf{x} \rightarrow \partial V_w
\]

Figure 3: Interface phenomena. The active (conductive) particle is depicted in light (dark) gray whereas the electrolyte ideally fills the picture background.
for π a generic field (either potential or stress and displacements) and for \( w = e, a, c \). The outward normal direction on surface \( \partial V_w \) will be denoted with \( \mathbf{n}_w \).

At the interface between active particles and conductive particles \( \partial V_e \cap \partial V_a \), electrons are free to flow without causing discontinuities in the electric field and in potentials \( \phi, \mathbf{\overline{E}}_e \). Neutral Lithium does not intercalate into conductive particles. Continuity of displacements and surface tractions are imposed.

\[
\begin{align*}
\mathbf{h}_a^{m \cdot} \cdot \mathbf{n}_a |_{\partial V_a} & = 0 \quad x \in \partial V_e \cap \partial V_a \\
\mathbf{h}_a^{m \cdot} \cdot \mathbf{n}_a = \mathbf{h}_a^{m \cdot} \cdot \mathbf{n}_c |_{\partial V_a} & = 0 \quad x \in \partial V_e \cap \partial V_a \\
\mathbf{\overline{E}}_{c\cdot} |_{\partial V_a} = \mathbf{\overline{E}}_{c\cdot} |_{\partial V_c} & = 0 \quad x \in \partial V_e \cap \partial V_a \\
\mathbf{E}^m \cdot \mathbf{n}_a |_{\partial V_a} & = \mathbf{E}^m \cdot \mathbf{n}_c |_{\partial V_a} \quad x \in \partial V_e \cap \partial V_a \\
\phi^m |_{\partial V_a} & = \phi^m |_{\partial V_c} \quad x \in \partial V_e \cap \partial V_a \\
\mathbf{u}^m |_{\partial V_a} & = \mathbf{u}^m |_{\partial V_c} \quad x \in \partial V_e \cap \partial V_a \\
\sigma^m \mathbf{n}_a |_{\partial V_a} & = \sigma^m \mathbf{n}_c |_{\partial V_a} \quad x \in \partial V_e \cap \partial V_a
\end{align*}
\]

At the interface between electrolyte and conductive particles \( \partial V_e \cap \partial V_c \), there is no intercalation neither of Li-ions nor of counterions. Electrons do not flow through the interface. Continuity of displacements and surface tractions are imposed.

\[
\begin{align*}
\mathbf{h}_{Li^+}^{m \cdot} \cdot \mathbf{n}_e |_{\partial V_c} & = 0 \quad x \in \partial V_e \cap \partial V_c \\
\mathbf{h}_{X^-}^{m \cdot} \cdot \mathbf{n}_c |_{\partial V_c} & = 0 \quad x \in \partial V_e \cap \partial V_c \\
\mathbf{h}_{\cdot}^{m \cdot} \cdot \mathbf{n}_c |_{\partial V_c} & = 0 \quad x \in \partial V_e \cap \partial V_c \\
\mathbf{E}^m \cdot \mathbf{n}_e |_{\partial V_c} & = \mathbf{E}^m \cdot \mathbf{n}_c |_{\partial V_c} \quad x \in \partial V_e \cap \partial V_c \\
\phi^m |_{\partial V_c} & = \phi^m |_{\partial V_c} \quad x \in \partial V_e \cap \partial V_c \\
\mathbf{u}^m |_{\partial V_c} & = \mathbf{u}^m |_{\partial V_c} \quad x \in \partial V_e \cap \partial V_c \\
\sigma^m \mathbf{n}_c |_{\partial V_c} & = \sigma^m \mathbf{n}_c |_{\partial V_c} \quad x \in \partial V_e \cap \partial V_c
\end{align*}
\]

At the interface between electrolyte and active particles \( \partial V_e \cap \partial V_a \), there is no intercalation of X-anions, whereas a Faradaic reaction converts the oxidized Lithium to its neutral state before its diffusion into the active particles lattice. Electrode kinetics is here modeled via the Butler-Volmer equation (36), in terms of thermodynamic excess \( \gamma \) and surface over potential \( \chi \) defined in equations (34, 35). It will be denoted with

\[
\begin{align*}
h_{BV} & = \frac{i_0}{F} \\left\{ \exp \left[ \frac{1 - \beta}{R \cdot \vartheta} \frac{\gamma}{F} \right] - \exp \left[ - \frac{\beta}{R \cdot \vartheta} \frac{\gamma}{F} \right] \right\} \\
i_{BV} & = i_0 \left\{ \exp \left[ \frac{1 - \beta}{R \cdot \vartheta} \frac{\chi}{F} \right] - \exp \left[ - \frac{\beta}{R \cdot \vartheta} \frac{\chi}{F} \right] \right\}
\end{align*}
\]

Continuity of displacements and surface tractions are imposed.

\[
\begin{align*}
\mathbf{h}_{Li^+}^{m \cdot} \cdot \mathbf{n}_e |_{\partial V_a} & = -h_{BV} \quad x \in \partial V_a \cap \partial V_e \\
\mathbf{h}_a^{m \cdot} \cdot \mathbf{n}_a |_{\partial V_a} & = h_{BV} \quad x \in \partial V_a \cap \partial V_e \\
\mathbf{h}_a^{m \cdot} \cdot \mathbf{n}_a |_{\partial V_a} & = -h_{BV} \quad x \in \partial V_a \cap \partial V_e \\
\mathbf{h}_a^{m \cdot} \cdot \mathbf{n}_c |_{\partial V_a} & = 0 \quad x \in \partial V_a \cap \partial V_e \\
\mathbf{E}^m + \frac{1}{\varepsilon_0} \mathbf{1}^m \cdot \mathbf{n}_a |_{\partial V_a} & = \frac{i_{BV}}{\varepsilon_0} \quad x \in \partial V_a \cap \partial V_e \\
\mathbf{E}^m + \frac{1}{\varepsilon_0} \mathbf{1}^m \cdot \mathbf{n}_a |_{\partial V_a} & = \frac{i_{BV}}{\varepsilon_0} \quad x \in \partial V_a \cap \partial V_e \\
\mathbf{u}^m |_{\partial V_a} & = \mathbf{u}^m |_{\partial V_a} \quad x \in \partial V_a \cap \partial V_e \\
\sigma^m \mathbf{n}_a |_{\partial V_a} & = \sigma^m \mathbf{n}_a |_{\partial V_a} \quad x \in \partial V_a \cap \partial V_e
\end{align*}
\]
7.3 Scales transitions and weak form

Define the volume ratios of each microscopic phase with respect to the overall microscopic volume $V$ of the RVE.

$$\epsilon_e = \frac{V_e}{V}, \quad \epsilon_a = \frac{V_a}{V}, \quad \epsilon_c = \frac{V_c}{V}$$

(65)

$\epsilon_e$ is usually termed the porosity of the electrode material. It will be denoted also with $\epsilon_E = \epsilon_e + \epsilon_c = V_E/V$, where $V_E = V_a + V_c$ is the volume of the electrode at the micro scale. Porosity can actually be considered a macroscopic property, being uniquely defined at each point of the macroscopic domain $\Omega_{Ca}$ on the basis of the underlying microstructure. For the sake of readiness however apex will be omitted on $\epsilon$.

In the computational homogenization scheme at hand two main assumptions will be made, namely the steady-state mass and charge transport hypothesis at the microscale and the electroneutrality. The former is a usual assumption in multi scale time-dependent problems [28, 29] in order to perform a computational homogenization scheme without time-scale transitions. A steady-state mass and charge transport is justified as steady-state is instantaneous changes for concentration and potentials at the micro scale, which are dictated through the boundary conditions that originate from the time-dependent macro scale problem.

Electroneutrality is a generally accepted assumption in battery cell modeling, according to Newman’s theory [24]. It is here invoked to circumvent the issues due to the body forces and bulk charges distributions. As well known, the presence of bulk terms in homogenization theory pose still unsolved problems.

7.3.1 Macro to micro scales transitions

A first order theory is adopted for mechanical and electrochemical homogenization procedures, stemming from the principle of scales separation. As for the weak forms, the problem will be formulated in terms of an independent variable set $y$ that includes the following fields: displacements $u^m$, chemical $\mu^m$, electrochemical $\pi^m$, $p_{ex}^m$, $p_{ei}^m$, and electric $\phi^m$, $\phi_e^m$ potentials. They can be decomposed without loss of generality at the microscale domain and in a microfluctuation field, denoted with the symbol $\tilde{\pi}$

$$\pi^m(x) = \pi^m(x^{ref}) = \nabla \left[ \pi^M \right] \cdot (x - x^{ref}) + \tilde{\pi}(x), \quad x \in V_\gamma$$

(66)

denoting with the symbol $\pi$ a generic field in $y$. Microscopic fields in (66) refer to their values at a reference point $x^{ref}$.

The displacement field at reference point $x^{ref}$ is set to zero in order to eliminate the rigid body translation; the rigid body rotation will be suppressed through the microscopic boundary conditions introduced further in section 7.3.2. A scale transition of “order zero” must be enforced for jumps $\gamma^m = \mu^m_{Li} - \tilde{p}_{ex}^m - \tilde{p}_{Li}^m$, $\xi^m = \phi^m_e - \phi^m_e$.

The following average condition is enforced for $\gamma$:

$$\gamma^M = \mu^M_{Li} - \tilde{p}_{ex}^M - \tilde{p}_{Li}^M = \frac{1}{V_a} \int_{V_a} \mu_{Li}^m dV - \frac{1}{V_E} \int_{V_E} \tilde{p}_{ex}^m dV - \frac{1}{V_c} \int_{V_c} \tilde{p}_{Li}^m dV$$

(67)

together with the assumption

$$\gamma^m(x^{ref}) = \gamma^M$$

(68)

By the linearization (66) the integral constraint

$$\frac{1}{V_a} \int_{V_a} \tilde{\mu}_{Li}(x) dV - \frac{1}{V_E} \int_{V_E} \tilde{\tilde{p}}_{ex}^m (x) dV - \frac{1}{V_c} \int_{V_c} \tilde{\tilde{p}}_{Li}^m (x) dV =$$

$$\frac{1}{V_a} \int_{V_a} \nabla \left[ \mu^M_{Li} \right] \cdot (x - x^{ref}) dV - \frac{1}{V_E} \int_{V_E} \nabla \left[ \tilde{p}_{ex}^M \right] \cdot (x - x^{ref}) dV - \frac{1}{V_c} \int_{V_c} \nabla \left[ \tilde{p}_{Li}^M \right] \cdot (x - x^{ref}) dV$$

Diffusive processes scales as $1/L^2$, being $L$ the length scale [48]. The time for a particle to reach the steady state when concentration is changed scales as $1/L^2$. 

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has to be satisfied. One could for instance enforce
\[ \int_{V_a} \tilde{\mu}_{Li}(x) \, dV = 0 , \quad \int_{V_E} \tilde{\mu}_{e-}(x) \, dV = 0 , \quad \int_{V_e} \tilde{\mu}_{Li+}(x) \, dV = 0 \]
whence the constraint on the position of the reference point \( \mathbf{x}^{ref} \)
\[ \frac{1}{V_a} \nabla \left[ \mu_{Li}^M \right] \cdot \int_{V_a} \mathbf{x} - \mathbf{x}^{ref} \, dV - \frac{1}{V_E} \nabla \left[ \mu_{Li}^M \right] \cdot \int_{V_E} \mathbf{x} - \mathbf{x}^{ref} \, dV - \frac{1}{V_e} \nabla \left[ \mu_{Li}^M \right] \cdot \int_{V_e} \mathbf{x} - \mathbf{x}^{ref} \, dV = 0 \]
and the constraints on the microscopic fields
\[ \int_{V_a} \mu_{Li}^m(\mathbf{x}) - \mu_{Li}^m(\mathbf{x}^{ref}) - \nabla \left[ \mu_{Li}^M \right] \cdot (\mathbf{x} - \mathbf{x}^{ref}) \, dV = 0 \] (69a)
\[ \int_{V_E} \pi_{Li}^m(\mathbf{x}) - \pi_{Li}^m(\mathbf{x}^{ref}) - \nabla \left[ \pi_{Li}^M \right] \cdot (\mathbf{x} - \mathbf{x}^{ref}) \, dV = 0 \] (69b)
\[ \int_{V_e} \mu_{Li+}^m(\mathbf{x}) - \mu_{Li+}^m(\mathbf{x}^{ref}) - \nabla \left[ \mu_{Li+}^M \right] \cdot (\mathbf{x} - \mathbf{x}^{ref}) \, dV = 0 \] (69c)

The same path of reasoning can be applied to \( \xi \), under the assumption
\[ \xi^m(\mathbf{x}^{ref}) = \xi^M \] (70)

“Order one” scale transition conditions on the average values of the gradients of the independent variable fields must be enforced
\[ \nabla \left[ \pi^M \right] = \frac{1}{V_a} \int_{V_a} \nabla \left[ \pi^m \right] \, dV \] (71)
leading to a set of integral constraints on the microfluctuation fields:
\[ \int_{V_a} \nabla \left[ \pi^m \right] \, dV = \int_{\partial V_a} \pi^m \otimes \mathbf{n} = 0 \] (72)
which will be satisfied through the definition of proper boundary conditions for fields \( \pi \) along \( \partial V_a \). They are discussed in the next Section.

### 7.3.2 Micro scale boundary conditions

Different kinds of microscopic boundary conditions may arise from constraint (72). Classical ones are Taylor, Linear displacements, Minimal Kinematical or Tractionss, Periodic [37, 38]. In this contribution periodic boundary conditions will be applied on the microfluctuation displacement field \( \tilde{\mathbf{u}} \). Denoting with \( l \) the side length of the square RVE, and with \( \partial^L V \) and \( \partial^B V \) its left and bottom sides, the periodic boundary conditions read:
\[ \tilde{\mathbf{u}}(\mathbf{x}) = \tilde{\mathbf{u}}(\mathbf{x} + l \mathbf{e}_1) \quad \mathbf{x} \in \partial^L V \] (73a)
\[ \tilde{\mathbf{u}}(\mathbf{x}) = \tilde{\mathbf{u}}(\mathbf{x} + l \mathbf{e}_2) \quad \mathbf{x} \in \partial^B V \] (73b)
or, equivalently, in terms of the displacement field \( \mathbf{u}^m \)
\[ \mathbf{u}^m(\mathbf{x} + l \mathbf{e}_1) - \mathbf{u}^m(\mathbf{x}) = l \, \varepsilon^M \mathbf{e}_1 \quad \mathbf{x} \in \partial^L V \] (74a)
\[ \mathbf{u}^m(\mathbf{x} + l \mathbf{e}_2) - \mathbf{u}^m(\mathbf{x}) = l \, \varepsilon^M \mathbf{e}_2 \quad \mathbf{x} \in \partial^B V \] (74b)

Extension to three dimensional RVEs is trivial.

The boundary conditions for the electrochemical and electric potentials have to be formulated in a different way because the boundary of each phase does not coincide with the external RVE boundary. Constraint (72) specifies as
\[ \int_{\partial V_a} \tilde{\mu}_{Li+} \, \mathbf{n} \, d\Gamma = 0 , \quad \int_{\partial V_a} \tilde{\mu}_{X-} \, \mathbf{n} \, d\Gamma = 0 , \quad \int_{\partial V_a} \tilde{\mu}_{Li} \, \mathbf{n} \, d\Gamma = 0 , \quad \int_{\partial V_e} \tilde{\mu}_{e-} \, \mathbf{n} \, d\Gamma = 0 \] (75)
\[
\int_{\partial V_e} \tilde{\phi}_e \, n \, d\Gamma = 0 , \quad \int_{\partial V_e} \tilde{\phi}_E \, n \, d\Gamma = 0 \quad (76)
\]

The constraints are imposed along the interfaces \(\partial V_j \cap \partial V_e, \ i, j = a, e, E\) as well as along the sides of the RVE, \(\partial V_j \cap \partial V_j, \ j = a, e, E\). The easiest way to satisfy (75-76) is the so-called Taylor approach, setting vanishing fluctuations along the interfaces and the RVE boundary

\[
\mu_{Li}|_{\partial V_e} = \rho_{X-}|_{\partial V_e} = \mu_{Li}|_{\partial V_e} = \tilde{\phi}_E|_{\partial V_e} = \hat{\phi}_e|_{\partial V_e} = 0 \quad (77)
\]

In terms of microscopic fields

\[
\begin{align*}
\mu_{Li}^N(x) &= \nabla \left[ \mu_{Li}^M \right] \cdot (x-x^{ref}) + \mu_{Li}^N(x^{ref}) \quad x \in \partial V_e \quad (78a) \\
\mu_{X}^N(x) &= \nabla \left[ \mu_{X}^M \right] \cdot (x-x^{ref}) + \mu_{X}^N(x^{ref}) \quad x \in \partial V_e \quad (78b) \\
\phi_{E}^N(x) &= \nabla \left[ \phi_{E}^M \right] \cdot (x-x^{ref}) + \phi_{E}^N(x^{ref}) \quad x \in \partial V_e \quad (78d) \\
\phi_{e}^N(x) &= \nabla \left[ \phi_{e}^M \right] \cdot (x-x^{ref}) + \phi_{e}^N(x^{ref}) \quad x \in \partial V_e \quad (78f)
\end{align*}
\]

### 7.3.3 Weak form

The weak form for the microscale problem can be given in terms of the potentials, displacements, and concentrations in a time interval \([0, T]\) as

Find \(y^m \in V^{[0, T]}\) such that

\[
\frac{d}{dt} b(\hat{y}^m(t), \hat{y}^m) + a(y^m(t), \hat{y}^m) = f(\hat{y}^m) \quad \forall \hat{y}^m \in V \quad (79)
\]

As for the macro scale, the identification of the functional spaces \(V^{[0, T]}, V\) falls beyond the scope of the present note. Vectors \(z^m\) and \(y^m\) collect the time-dependent unknown fields and are defined as for the macro scale with reference to the micro scale fields. Vector \(\hat{y}^m\) collects the steady-state test functions that correspond to the unknown fields in \(y^m\). Vector \(z^m\) is now dependent on \(y^m\) by constitutive equations, as the ones derived from the Landau potential (30). The governing equations are properly formulated in strong and weak form. Ellipticity of operators, functional and numerical properties of the solution and of its approximation depend on the constitutive assumptions and on the choice of the correct functional spaces \(V^{[0, T]}, V\). Bilinear forms \(a(\cdot, \cdot)\) and \(b(\cdot, \cdot)\) are defined as

\[
\begin{align*}
b(\hat{y}^m, z^m) &= -\int_{\Omega} \mu_{Li}^N \cdot c_{Li} \, d\Omega - \int_{\Omega} \mu_{X}^N \cdot c_{X} \, d\Omega - \int_{\Omega} \mu_{E}^N \cdot c_{E} \, d\Omega - \int_{\Omega} \mu_{Li}^m \cdot c_{Li} \, d\Omega + \int_{\Omega} \mu_{X}^m \cdot c_{X} \, d\Omega + \int_{\Omega} \mu_{E}^m \cdot c_{E} \, d\Omega \quad (80) \\
a(y^m, \hat{y}^m) &= \int_{\Omega} \nabla [(\nabla \mu_{Li}^m) \cdot h_{Li}^m] \, d\Omega + \int_{\Omega} \nabla [(\nabla \mu_{X}^m) \cdot h_{X}^m] \, d\Omega + \int_{\Omega} \nabla [(\nabla \mu_{E}^m) \cdot h_{E}^m] \, d\Omega \\
&+ \int_{\Omega} \nabla [(\phi_{Li}^m) \cdot E_{Li}^m] \, d\Omega + \int_{\Omega} \nabla [(\phi_{X}^m) \cdot E_{X}^m] \, d\Omega + \int_{\Omega} \nabla [(\phi_{E}^m) \cdot E_{E}^m] \, d\Omega \\
&+ \int_{\Omega} \sigma^m \cdot \varepsilon^m \, d\Omega + \int_{\Omega} F \cdot c_{Li}^m \cdot E_{Li}^m \cdot \hat{u}^m \, d\Omega + \int_{\Omega} F \cdot c_{X}^m \cdot E_{X}^m \cdot \hat{u}^m \, d\Omega - \int_{\Omega} h_{BV} \hat{y}^m \, d\Omega - \int_{\partial V_e \cap \partial V_e} \frac{1}{\varepsilon_0} i_{BV} \hat{\varepsilon}^m \, d\Gamma \quad (81)
\end{align*}
\]

The given terms are due to the electrostatic interactions in the bulk

\[
f(\hat{y}^M) = \int_{\Omega} F \cdot c_{Li}^m \cdot E_{Li}^m \cdot \hat{u}^m \, d\Omega \quad (82)
\]
7.3.4 Micro to macro scales transitions

The homogenized macroscopic quantities are extracted from the solution of the microscale problem and upscaled. The micro to macro scale transition is achieved by extending the Hill-Mandel condition (6), namely the balance between microscopic volume average of the virtual power on the RVE and the “point wise” one at the macroscale. In view of the choice made in the present note of assuming as independent variable fields the potentials rather than the concentrations, the power expenditure can be easily recognized within the weak form. The time-dependent part of the expenditure is enclosed in bilinear form \( a(\cdot, \cdot) \). It will be assumed that the micro to macro scale transition pertain to the time independent power expenditure only, as if the micro scale problem would be steady state in the sense explained already. Therefore only bilinear form \( a(\cdot, \cdot) \) is of interest in this regard. The assumption of electroneutrality will be embraced. Such an assumption is customary in battery modeling, for the charge distribution effects on the power expenditure are usually taken as secondary. Accordingly, in bilinear form \( a(\cdot, \cdot) \) all contributions due to bulk interactions must be neglected. Denoting with hatted quantities the virtual velocity fields, the extended Hill-Mandel condition thus reads

\[
\int_{V_{\varepsilon}} \nabla \left( \hat{\mu}^M_{Li} \right) \cdot \mathbf{h}^M_{Li} \, d\Omega + \int_{V_{\varepsilon}} \nabla \left[ \hat{\mu}^M_{c_e} \right] \cdot \mathbf{h}^M_{c_e} \, d\Omega + \int_{V_{\varepsilon}} \nabla \left[ \hat{\mu}^M_{Li^+} \right] \cdot \mathbf{h}^M_{Li^+} + \nabla \left[ \hat{\mu}^M_{X^-} \right] \cdot \mathbf{h}^M_{X^-} \, d\Omega + \\
\int_{V_{\varepsilon}} \nabla \left[ \hat{\mu}^M_{E} \right] \cdot \mathbf{N}^M_{E} \, d\Omega + \int_{V_{\varepsilon}} \nabla \left[ \hat{\mu}^M_{c_e} \right] \cdot \mathbf{N}^M_{c_e} \, d\Omega + \int_{V} \sigma^M \cdot \hat{\varepsilon}^M \, d\Omega - \int_{\partial V_{\varepsilon} \cap \partial V_{c_e}} h_{BV} \hat{\varepsilon}^M \, d\Gamma + \\
- \int_{\partial V_{\varepsilon} \cap \partial V_{c_e}} \frac{1}{\varepsilon_0} i_{BV} \hat{\xi}^M \, d\Gamma = \varepsilon_E \nabla \left[ \hat{\gamma}^M_{E} \right] \cdot \mathbf{N}^M_{E} + \varepsilon_E \nabla \left[ \hat{\gamma}^M_{c_e} \right] \cdot \mathbf{N}^M_{c_e} + \sigma^M \cdot \hat{\varepsilon}^M + \hat{h}_{Li} \left( \hat{\gamma}^M + \frac{\hat{F} \hat{\xi}^M}{\varepsilon_0} \right) + \\
\varepsilon_E \left( \nabla \left[ \hat{\mu}^M_{Li} \right] \cdot \mathbf{h}^M_{Li} + \nabla \left[ \hat{\mu}^M_{c_e} \right] \cdot \mathbf{h}^M_{c_e} \right) + \varepsilon_e \left( \nabla \left[ \hat{\mu}^M_{Li^+} \right] \cdot \mathbf{h}^M_{Li^+} + \nabla \left[ \hat{\mu}^M_{X^-} \right] \cdot \mathbf{h}^M_{X^-} \right)
\]

having set \( \hat{\varepsilon} = \hat{E} + \frac{1}{\varepsilon_0} \hat{I} \) for the sake of conciseness. By means of linearization (66), applying the divergence theorem and the chain rule, finally taking into account electroneutrality and equilibrium equation (62), the mechanical contribution in identity (83) can be written as

\[
\frac{1}{V} \int_{V} \sigma^m \cdot \hat{\varepsilon}^m \, dV = \frac{1}{V} \int_{V} \sigma^m \, dV \cdot \hat{\varepsilon}^M + \frac{1}{V} \int_{\partial V} \mathbf{t}^m \cdot \hat{\mathbf{u}} \, d\Gamma = \frac{1}{V} \int_{V} \sigma^m \, dV \cdot \hat{\varepsilon}^M
\]

due to the anti-periodicity of the tractions \( \mathbf{t}^m = \sigma n \) over the boundary of the RVE. The virtual power due to the electrode kinetics at the interface \( \partial V_{\varepsilon} \cap \partial V_{c_e} \) between active particles and the electrolyte can be restated noting that \( \gamma \) is by definition a linear combination of potentials, to which linearization (66) applies. Therefore, the same linearization holds for \( \gamma \), if taken in the sense of limit of internal linearized fields. It holds then

\[
\int_{\partial V_{\varepsilon} \cap \partial V_{c_e}} h_{BV} \hat{\varepsilon}^m \, d\Gamma = \int_{\partial V_{\varepsilon} \cap \partial V_{c_e}} h_{BV} \, d\Gamma \hat{\gamma}^M + \int_{\partial V_{\varepsilon} \cap \partial V_{c_e}} h_{BV} (\mathbf{x} - \mathbf{x}^{ref}) \, d\Gamma \cdot \nabla \left[ \gamma^M \right]
\]

in view of Taylor boundary conditions on the micro fluctuation and of assumption (68). By the same path of reasoning, it holds

\[
\int_{\partial V_{E} \cap \partial V_{c_e}} i_{BV} \hat{\xi}^m \, d\Gamma = \int_{\partial V_{E} \cap \partial V_{c_e}} i_{BV} \, d\Gamma \hat{\xi}^M + \int_{\partial V_{E} \cap \partial V_{c_e}} i_{BV} (\mathbf{x} - \mathbf{x}^{ref}) \, d\Gamma \cdot \nabla \left[ \xi^M \right]
\]

owing to (70). Again taking into account the Taylor boundary conditions on the micro fluctuation it comes out

\[
\int_{V_{\varepsilon}} \nabla \left[ \hat{\mu}^M_{Li} \right] \cdot \mathbf{h}^M_{Li} \, dV = \int_{V_{\varepsilon}} \mathbf{h}^M_{Li} \, dV \cdot \nabla \left[ \hat{\mu}^M_{Li} \right] + \int_{V_{\varepsilon}} \nabla \left[ \hat{\mu}^M_{Li^+} \right] \cdot \mathbf{h}^M_{Li^+} \, dV = \int_{V_{\varepsilon}} \mathbf{h}^M_{Li} \, dV \cdot \nabla \left[ \hat{\mu}^M_{Li} \right]
\]

in view of the (steady-state) mass balance equation (53). The previous path of reasoning applies to the electrochemical and to the electrostatic potentials contributions in equation (83) as well.

By comparing the corresponding power contributions into the Hill-Mandel condition (83), the following micro to macro scale transitions are finally obtained:

\[
\sigma^M = \frac{1}{V} \int_{V} \sigma^m \, dV
\]
\[ \epsilon_E h^M_{Li} = \int_{V_a} h^m_{Li} \, dV_a - \int_{\partial V_a \cap \partial V_e} h_{BV} \left( x - x^{ref} \right) \, d\Gamma \quad (88b) \]

\[ \epsilon_E h^M_{_e} = \int_{V_e} h^m_{_e} \, dV_e + \int_{\partial V_a \cap \partial V_e} h_{BV} \left( x - x^{ref} \right) \, d\Gamma \quad (88c) \]

\[ \epsilon_{L_i} h^M_{Li+} = \int_{V_a} h^m_{Li+} \, dV_a + \int_{\partial V_a \cap \partial V_e} h_{BV} \left( x - x^{ref} \right) \, d\Gamma \quad (88d) \]

\[ \epsilon_{X_-} h^M_{X-} = \int_{V_e} h^m_{X-} \, dV_e \quad (88e) \]

\[ \epsilon_{E} h^M_{E} = \int_{V_e} \frac{\nabla^m_e}{\varepsilon_0} \, dV_e - \int_{\partial V_a \cap \partial V_e} \frac{i_{BV}}{\varepsilon_0} \left( x - x^{ref} \right) \, d\Gamma \quad (88f) \]

\[ \epsilon_{e} h^M_{e} = \int_{V_e} \frac{\nabla^m_e}{\varepsilon_0} \, dV_e + \int_{\partial V_a \cap \partial V_e} \frac{i_{BV}}{\varepsilon_0} \left( x - x^{ref} \right) \, d\Gamma \quad (88g) \]

\[ \tilde{h}_{Li} = - \int_{\partial V_a \cap \partial V_e} h_{BV} \, d\Gamma \quad (88h) \]

\[ F \tilde{h}_{Li} = - \int_{\partial V_a \cap \partial V_e} i_{BV} \, d\Gamma \quad (88i) \]

Average identities (88h, 88i) envisage a further constraint on \( h_{BV} \) and \( i_{BV} \). Such a constraint must have a constitutive origin because relates electrochemical and electric potentials. After imposing constitutive prescriptions, it is well known from the literature that identity

\[ \chi = \frac{1}{F} \gamma \]

comes out (see [49] and also appendix 0, formula (102)). The latter, together with the interface condition \( \xi = 0 \) that has been assumed along \( \partial V_a \cap \partial V_e \) are the required constraints on \( h_{BV} \) and \( i_{BV} \).

For the resolution of the macroscopic boundary value problem the concentration is needed in bilinear form \( b(\cdot, \cdot) \) at each increment: an additional micro-to-macro scale transition is required in order to evaluate \( c^M \), based on the conservation of mass through the scales and of the Landau potential.

\[ c^M_{Li} = \frac{1}{V_a} \int_{V_a} c^m_{Li} \, dV_a \quad (89a) \]

\[ c^M_{Li+} = \frac{1}{V_a} \int_{V_a} c^m_{Li+} \, dV_a \quad (89b) \]

\[ c^M_{X-} = \frac{1}{V_e} \int_{V_e} c^m_{X-} \, dV_e \quad (89c) \]

\[ c^M_{e} = \frac{1}{V_E} \int_{V_E} c^m_{e} \, dV_E \quad (89d) \]

8 Hints on the solution procedure

8.1 Discretization

The macroscale weak form (49) can be written in the following semi-discrete (continuous in time) approximated form

\[ \text{Find } y^M_h \in V^0_h[T] \text{ such that} \]

\[ \frac{d}{dt} b \left( x^M_h(t), \dot{y}^M_h \right) + a(y^M_h(t), \ddot{y}^M_h) = f(t, \dot{y}^M_h) \quad \forall \ddot{y}^M_h \in V_h, \ t \in (0, T) \quad (90) \]

with \( y^M_h(0) = y_{0,h} \) an approximation of the initial datum. The Galerkin approximation for the steady problem using as \( V_h \) the classical finite element space is not satisfactory when advection is much stronger.
than diffusion, as the approximate solution is highly oscillatory unless the mesh size $h$ is sufficiently small. Advection-dominated problems require special care which is deferred to devoted investigations.

As motivated in the previous section, homogenization issues suggest to restrict the micro scale approximation to steady-state mass and charge transport under the hypothesis of electroneutrality. The discrete weak form of (79) becomes:

$$\text{Find } y^m \in V_h \text{ such that } a(y^m, \hat{y}^m) = f(\hat{y}^m) \quad \forall \hat{y}^m \in V_h$$

(91)

with $V_h$ the classical finite element space.

### 8.2 Time advancing by finite differences

A family of time-advancing methods based on the so-called $\theta$-scheme can be built for the macro scale discrete problem (90). For the sake of readability the apex $^M$ will be omitted without inducing any confusion, as the micro scale problem is taken as time-independent.

$$\frac{1}{\Delta t} b (z_h^{n+1} - z_h^n, \dot{y}_h) + a(\theta y_h^{n+1} + (1-\theta) y_h^n, \dot{y}_h) = \theta f(t_{n+1}, \dot{y}_h) + (1-\theta) f(t_n, \dot{y}_h) \quad \forall \dot{y}_h \in V_h$$

(92)

for each $n = 0, 1, \ldots, N-1$, where $0 \leq \theta \leq 1$, $\Delta t = T/N$ is the time step, $N$ is a positive integer and $y_h^n \in V_h$ is a suitable approximation of the initial datum. This includes the forward Euler scheme ($\theta = 0$), backward Euler ($\theta = 1$), and Crank-Nicolson ($\theta = 1/2$).

### 8.3 Newton-Raphson scheme

Depending on the constitutive assumptions, equations (91) and (92) can be non linear in $y_h^m$, $y_h^{n+1}$ respectively, which is the usual case. In particular equation (92) may be solved by means of the Newton Raphson iterative method. Define function $g(y_h^{n+1})$ as

$$g(y_h^{n+1}) = \frac{1}{\Delta t} b (z_h^{n+1} - z_h^n, \varphi_j) + a(\theta y_h^{n+1} + (1-\theta) y_h^n, \varphi_j) - [\theta f(t_{n+1}, \varphi_j) + (1-\theta) f(t_n, \varphi_j)]$$

$\{\varphi_j | j = 1, \ldots, N_h\}$ being a basis for $V_h$ and pose $\mathbf{x} = y_h^{n+1}$ for the sake of readability. Equation (92) reads

$$g(\mathbf{x}) = 0$$

(93)

and the Newton Raphson iterative scheme in an abstract formalism can be obtained by making recourse to the notion of Gateaux derivative. Taking $\epsilon \in \mathbb{R}$ it reads:

$$g(\mathbf{x}^{k+1}) = g(\mathbf{x}^k) + \frac{d}{d\epsilon} g(\mathbf{x}^k + \epsilon \Delta \mathbf{x}^k) \bigg|_{\epsilon=0} = 0$$

(94)

to be solved for increment $\Delta \mathbf{x}^k$ iteratively until its norm is sufficiently small. Within the computational homogenization procedure, the macroscopic Cauchy stress, mass fluxes, and electric fields are recovered from the numerical solution of the micro-scale problem (91) defined on the underlying microstructure (RVE) by means of micro to macro scale transitions (88). The Newton-Raphson iteration (94) requires macroscopic tangents. Their consistent derivation can be achieved in analogy with the scheme proposed in [28, 29] for thermo-mechanical analysis of heterogeneous solids.

### 9 Conclusions

A two-scale modeling of several electrochemical and mechanical processes that take place during charging/discharging cycles in Li-ion battery electrodes has been investigated in the present note. The performance of batteries relies on the interaction between micro and nano-scale phenomena, in particular within the electrodes. Intercalation, swelling and the consequent eventual mechanical failure originate at the nano-scale, where neutral Lithium is inserted or extracted from active particles. Modeling all particles in the electrodes is unfeasible, because of the computational cost of the numerical approximation. Therefore, the nano-scale effects are usually incorporated into a micro-scale modelization through averages techniques and
constitutive models that are derived from homogenization methods. In the present contribution the computational homogenization has been formulated for the multi physics problem at hand. The key components of the scheme, i.e. the formulation of the microstructural boundary value problem and the coupling between the micro and macrolevel based on the averaging theorems, are addressed.

At the macro-scale, the electrode is considered as a porous continuum, whereas at the micro level it is heterogeneous and multiphase. The microscopic length scale is still much larger than the molecular dimensions, so that a continuum approach is justified for every constituent. The microscopic length scale, say the particle characteristic size, is three order of magnitudes smaller than the characteristic macroscopic length, that can be identified with the cell size. Therefore, the model is well framed into the principle of separation of scales.

The basic concepts of the proposed scheme, as established by Suquet [37], consist in the formulation of the microscopic boundary conditions from the macroscopic input variables (macro-to-micro transition) as well as in the calculation of the macroscopic output variables from the analysis of the deformed microstructural RVE (micro-to-macro transition). This two steps stem from a rigorous thermodynamic analysis, that firmly distinguished the balance and the constitutive contributions to the formulation. Furthermore, the Hill-Mandel condition [30] has been extended, so that the internal expenditure of virtual power of mechanical forces, of charge and mass fluxes is preserved in the scale transition. The variational framework here outlined greatly benefited from choosing potentials rather than concentration as independent field in the modelization. Weak forms keep the usual significance of power expenditure, key concept in a multi scale approach. The procedure itself is independent on the constitutive laws at the micro-scale, provided that thermodynamic restrictions discussed in section 5 are satisfied and that the microscopic boundary value problem admits a unique solution. In fact, constitutive theory was not provided so far. Supplementary material is provided in appendices, where simple constitutive laws are applied.

Processes in Li-ion batteries electrodes are modeled with the partial differential equations setting of diffusion-migration-intercalation problems and their mechanical coupling. It appears a new challenge for the computational homogenization technique. The (numerical) relation between the macroscopic input and output variables, particularly the tangent “stiffnesses” to be inserted in each incremental step of the Newton-Raphson scheme (94), have not been provided here but can be easily determined following the usual approach of the computational homogenization scheme: the reader may for instance refer to the scheme proposed in [28, 29] for thermo-mechanical analysis of heterogeneous solids.

Companion papers will be devoted to the implementation of the proposed scheme as well as to its extension to finite strain, taking special care to the proper configuration - either current or reference - in which the scale transitions shall be formulated. Being independent on the constitutive assumptions at the micro-scale, the most relevant ideas in the current impetuous development of constitutive modeling of the mechanical phenomena that take place during lithiation and delithiation, including plastic flow, phase segregation, damage, can be included in the solution scheme. In particular, degradation and growth of cracks, that have been largely observed in charging/discharging cycles in Li-ion battery electrodes, will be considered eventually following the approach in [50, 51, 52]. The binder, that has not been considered so far, could be included as a cohesive interface between particles and may play a fundamental role in modeling mass and charge transfer against a critical detachment of particles.

The computational homogenization scheme presented may provide a significant contribute to the multi physics simulation in the fundamental area of the mechanics of energy storage materials. If it will reach a sufficient maturity and robustness, the computational homogenization scheme can be attractive even for battery makers companies, interested in capturing a significant part of the expected strong increase in demand of Li-Ion batteries.

**Acknowledgements**

The present paper is the outcome of long time of training and discussions with several colleagues, professors, students. We are gratefully indebted with Prof. L. Anand, T. Wierzbicki, and Dr. C. Di Leo, with whom authors had long and fruitful discussions. The same applies to Prof. M. Geers, V. Kouznetsova who trained us on the computational homogenization technique. Ideas and remarks have been shared with Prof. A. Bower and his team at Brown University, whose work was extremely inspiring.
References


Appendix 1 - Constitutive theory

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The computational homogenization framework described in this paper applies to the most general constitutive theory, provided that thermodynamic restrictions discussed in section 5 are satisfied. The reader may feel unsatisfied though, because of the absence of constitutive specifications. She may doubt for intense that suitable form of the Landau potential can be written. To avoid such a disappointment, supplementary material is here provided. There are no novelties with respect to the large literature on the field. Furthermore, some assumptions are consciously simplistic. Exhaustive analysis on constitutive assumptions will be coupled with the implementation in further publications.

1.1 - Constitutive theory for the electrolyte

Following [18], the electrolyte will be idealized as an inviscid, incompressible fluid (i.e. a perfect fluid). Since the electrolyte fluid is incompressible, the small strain tensor must satisfy $\text{Tr}[\varepsilon] = 0$ and because of null viscosity the stress tensor has vanishing deviatoric part, i.e. $\sigma = p \mathbb{I}$. The pressure $p$ does not expend power internally and does not enter the entropy imbalance (12). In other words, the pressure is irrelevant to the internal thermodynamic structure of the theory and following [31] the pressure is not specified constitutively.

In the absence of charged species, only diffusion takes place; the relevant constitutive theory can be found in [31], section 66. In its dual way, in the absence of gradients of chemical potential diffusion cannot proceed. Current is thus driven by migration only and one expects the charge flux to be related to the electrostatic potential via Ohm’s law. When diffusion is present, a current density rises due to Faraday’s law and both processes contribute to the charge flux. It is therefore clear that concentration gradients and electric field acts contemporarily to generate ion mobility. This is the intimate nature of the electrochemical potential $\mu_{\alpha}$.

The chemical potential in a mixture depends on the composition of the mixture. It is convention to define ad “ideal” dependence of $\mu_{\alpha}$ on composition, and then to define a parameter called activity coefficient to describe the deviation of the actual electrochemical potential from the ideal. Ideal conditions are conventionally set in infinitely dilute solutions [24]. Therefore, in writing constitutive theories one firmly distinguishes the items of dilute and concentrated solutions in order to specify the thermodynamic potentials (either $\psi$ or $\Phi$) and to express the dependency of fluxes $h_{\alpha}$ in terms of appropriate driving forces for each ionic movement mechanism.

1.1.1 - Dilute solutions

One moves from restrictions (24) and assumes that the species flux $h_{\alpha}$ is given by a constitutive equation in terms of the electrochemical potential $\mu_{\alpha}$ and of concentration $c_{\alpha}$:

$$ h_{\alpha} = -M(c_{\alpha}) \nabla [\mu_{\alpha}] $$

i.e. one assumes a linear dependency of the mass flux of species $\alpha$ from the gradient of the electrochemical potential as usual in Fickian-diffusion. A classical specialization of mobility tensor $M(c_{\alpha})$ is the isotropic, linear choice

$$ M(c_{\alpha}) = u_{\alpha} c_{\alpha} \mathbb{I} $$

Definition (96) represents the physical requirement that the pure phase $c_{\alpha} = 0$ has vanishing mobility and there is no saturation limit for species $\alpha$ in the electrolyte. The amount $u_{\alpha} > 0$ is usually termed the ion mobility and represents the average velocity of species $\alpha$ in the solution when acted upon by a force of 1 N/mol independent of the origin of the force.

Infinitely dilute solutions. In “ideal”, infinitely diluted conditions the interactions between solutes are neglected. Only friction forces between the solute and the solvent are considered. The chemical interactions being ignored, an idealized electric potential that is the result of moving idealized electric charges from one electrode to the other can be taken as the electrostatic potential $\phi$. Ignoring the chemical environment that electrons experience, allows the complete separation of the phenomena of diffusion and migration in the mass transfer:

$$ \rho \dot{u}_{\text{diff}} = \sum_{\alpha} \mu_{\alpha} h_{\alpha} - \text{div}[\mu_{\alpha} h_{\alpha}] $$

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\[ \rho \dot{u}_{\text{migration}} = \sum_{\alpha} \phi i_{\alpha} - \text{div} \left[ \phi \mathbf{i}_{\alpha} \right] \]

In view of Faraday’s law (3) one writes
\[ \rho \left( \dot{u}_{\text{diff}} + \dot{u}_{\text{migration}} \right) = \sum_{\alpha} \left( \mu_{\alpha} + z_{\alpha} F \phi \right) h_{\alpha} - \text{div} \left[ \left( \mu_{\alpha} + z_{\alpha} F \phi \right) \mathbf{h}_{\alpha} \right] \] (97)
and by comparison with the mass flux contribution in (21) one splits the electrochemical potential of species \( \alpha \) in the sum
\[ \overline{\mu}_{\alpha} = \mu_{\alpha} + z_{\alpha} F \phi \] (98)
Such a splitting, with chemical potential \( \mu_{\alpha} \) merely depending on \( c_{\alpha} \), holds merely in ideal conditions.

To relate \( c_{\alpha} \) and \( \overline{\mu}_{\alpha} \) suitable specifications must be selected for the thermodynamic potentials. A free energy density \( \psi(c_{\alpha}) = \psi_{\text{diff}}(c_{\alpha}) + \psi_{\text{migr}}(c_{\alpha}, \phi) \) is given by a regular solution model for the continuum approximation to mixing
\[
\begin{align*}
\psi_{\text{diff}}(c_{\alpha}) &= \rho^{-1} \left( \mu_{\alpha}^0 c_{\alpha} + R \vartheta c_{\alpha} \log c_{\alpha} \right) \\
\psi_{\text{migr}}(c_{\alpha}, \phi) &= \rho^{-1} \left( z_{\alpha} F c_{\alpha} \phi \right)
\end{align*}
\] (99, 100)
with \( R \) the universal gas constant. Specialization (99) of Helmholtz’ free energy density represents the entropy of mixing for an ideal solution, with no energetic interactions. \( \mu_{\alpha}^0 \) is a reference value of the chemical potential of diffusing species \( \alpha \), taken as independent on the electric state, whereas it may depend on temperature and stress. Specialization (100) describes the migration contribution. Fick’s law (95) then becomes
\[ \mathbf{h}_{\alpha} = -u_{\alpha} R \vartheta \nabla \left[ c_{\alpha} \right] - z_{\alpha} F u_{\alpha} c_{\alpha} \nabla [\phi] \] (101)
which is the usual form for the flux density of species \( \alpha \) in absence of convection (see for instance [24], formula (11.1)) in dilute solutions. Defining the diffusion coefficient \( D_{\alpha} \) with \( D_{\alpha} = u_{\alpha} R \vartheta \) is nothing but the so called Nernst-Einstein equation.

In the Helmholtz free energy decomposition (99-100) no coupling with mechanical effects has been considered. This might be incorrect at high amounts of pressure in the electrolyte. Such a fundamental thermodynamical analysis goes beyond the scope of the present work.

In view of constitutive assumptions (99, 100) the potential imbalance \( \gamma \) defined in equation (35) reads
\[ \gamma = \mu_{\text{Li}} - \overline{\mu}_{\text{e}^-} = \mu_{\text{Li}}^0 - \mu_{\text{e}^-}^0 - \mu_{\text{Li}^+}^0 - R \vartheta + R \vartheta \log \frac{c_{\text{Li}}}{c_{\text{e}^-} + c_{\text{Li}^+}} + F \phi_{\text{e}^-} - F \phi_{\text{Li}^+} \]
At thermodynamic equilibrium \( \gamma = 0 \) and \( \xi = \xi^{\text{Nernst}} \), which implies
\[ \xi^{\text{Nernst}} = \frac{1}{F} \left( \mu_{\text{Li}}^0 - \mu_{\text{e}^-}^0 - \mu_{\text{Li}^+}^0 - R \vartheta + R \vartheta \log \frac{c_{\text{Li}}}{c_{\text{e}^-} + c_{\text{Li}^+}} \right) \]
thus
\[ \gamma = F \left( \xi - \xi^{\text{Nernst}} \right) = F \chi \] (102)

**Moderately diluted solutions.** In non ideal but moderately diluted solutions it is assumed again a linear dependency of the mass flux of species \( \alpha \) upon the gradient of the electrochemical potential of the same species, as in (95), ignoring cross-effects.

The main advantage of splitting (98), that once again holds in ideal conditions only, stands in its ability to characterize the electric state of a phase by means of an electric potential \( \phi \), that has the usual meaning of an electrostatic potential. The free energy density
\[ \psi(c_{\alpha}) = \psi_{\text{diff}}(c_{\alpha}) + \psi_{\text{dev}}(c_{\alpha}) + \psi_{\text{migr}}(c_{\alpha}, \phi) \]
is enriched with a a term \( \psi_{\text{dev}}(c_{\alpha}) \) that expresses a deviation from ideality in terms of the so called ionic activity coefficient \( f_{\alpha} \) that represents the energetic interactions of mixing\(^8\). One would like to relate \( f_{\alpha} \) to the yet undefined electric potential \( \phi \) in some way.

Modulo some unavoidable element of arbitrariness, see [24] chapter 3, an electric field potential can be properly defined. In order to assess the electrical state of a part of the system one usually refers to the reference electrode. But other choices are possible. A so called quasi-electrostatic potential \( \phi \) is defined by arbitrarily selecting an ionic species \( \beta \) and defining \( \phi \) as if in ideal conditions for \( \beta \):

\[
\mu_\beta = \mu_\beta^0 + z_\beta F \phi
\]

where \( \mu_\beta \), termed the quasi-chemical potential of species \( \beta \), is defined as to be the “ideal” chemical potential of species \( \beta \) by means of the usual thermodynamics restrictions without any activity coefficients, as from specialization (99). Then one has for any species \( \alpha \neq \beta \):

\[
\bar{\mu}_\alpha = \left( \frac{\mu_\alpha - \frac{z_\alpha}{z_\beta} \mu_\beta}{\frac{z_\alpha}{z_\beta} \mu_\beta} \right) + \frac{z_\alpha}{z_\beta} \mu_\beta + z_\alpha F \phi
\]

As the term in parentheses corresponds to a neutral combination of ions due to the electroneutrality condition, it must be independent on any definition of electric field. By taking specializations (99-100) for the free energy densities of species, and assuming as customary the following definition of activity coefficients:

\[
\frac{\partial \psi_{\text{dev}}}{\partial c_{\alpha}} = R \theta \log f_{\alpha}
\]

eye algebra leads to:

\[
\bar{\mu}_\alpha = R \theta \log c_{\alpha} + z_\alpha F \phi + R \theta \log f_\pm + \left( \mu_\alpha^0 - \frac{z_\alpha}{z_\beta} \mu_\beta^0 \right)
\]

with \( f_\pm = f_{\text{Li}^+} f_{\text{X}^-} \) usually termed mean activity coefficient - see [24], formula (2.25). At constant temperature, Fick’s law then becomes

\[
h_\alpha = -u_\alpha R \theta \nabla [c_{\alpha}] - z_\alpha F u_\alpha c_{\alpha} \nabla [\phi] - u_\alpha c_{\alpha} R \theta \nabla [\log f_\pm]
\]

that extends (101) to concentrated solutions. The mean activity coefficient is independent on the electric state and expresses the deviation from ideality of the chemical interactions.

The arbitrariness of the definition of the quasi-electrostatic potential stands in the need to choose an ionic species, but it conforms to the usual concept of electrostatic potential. In the limit of infinitely diluted solutions, the definition of \( \phi \) thus becomes independent on \( \beta \), consistently with the theory of diluted solutions.

Equation (103) is a sound extension of splitting (98) in non ideal cases. It requires a proper definition of the free energy \( \psi_{\text{dev}} \) to define the activity coefficients and their dependency upon the concentration. Equation (103) can also be easily inverted

\[
c_{\alpha} = \exp \left[ \frac{1}{R \theta} \left( \bar{\mu}_\alpha - \mu_\alpha^0 - z_\alpha F \phi \right) \right]
\]

having set \( \mu_\alpha^0 = \left( \mu_\alpha^0 - \frac{z_\alpha}{z_\beta} \mu_\beta^0 \right) + R \theta \log f_\pm \).

1.1.2 - Concentrated solutions.

Ficks law (95) states that the flux of phase \( \alpha \) is proportional to the gradient of the concentration of this species, directed against the gradient. There is no influence of the other phases, i.e. cross-effects are

\[
f_{\text{Li}^+} f_{\text{X}^-} \to 1 \quad \text{as} \quad (c_{\text{Li}^+} + c_{\text{X}^-}) \to 0
\]
ignored although well-known to appear in reality. To account for energetic interactions between phases, a multicomponent diffusion approach is required for realistic models. The standard approach [53] within the theory of Irreversible Thermodynamics replaces Fickian fluxes by linear combinations of the gradients of all involved electrochemical potentials. In the case of binary electrodes:

\[ h_{\alpha} = - \sum_{j=1}^{2} M_{\alpha \beta}(c_1, c_2) \nabla \left[ \phi_{\beta} \right] \quad \alpha = 1, 2 \]  

(106)

Mobility tensors \( M_{\alpha \beta}(c_1, c_2) \) on turn depend on the concentration of all phases. A classical specialization of such mobility tensors is an isotropic choice

\[ M_{\alpha \beta}(c_1, c_2) = M_{\alpha \beta}(c_1, c_2) c_{\alpha} 1 \]

whereas linearity is not usually assumed for \( M_{\alpha \beta}(c_1, c_2) \). The full matrix of mobility coefficients \( M_{\alpha \beta} \) has to be positive semi-definite in order to be consistent with thermodynamic restriction (24) and symmetric due to the Onsager reciprocal relations. The approach that provides specifications for \( M_{\alpha \beta} \) is usually known as Maxwell-Stefan approach [54] and is here described for the case of a binary electrolyte under the assumption of absence of convective motion of the solvent.

The Maxwell-Stefan approach assumes that the thermodynamical driving forces of the \( i \)-th species, namely \( c_i \nabla \left[ \phi_i \right] \), are in local equilibrium with the total friction force. The mutual friction force between species \( i \) and \( j \) is assumed to be proportional to the mass fluxes. The Maxwell-Stefan equations of multicomponent diffusion thus read:

\[ \frac{c_i}{R \theta} \nabla \left[ \phi_i \right] = - \sum_{j=0, 1, 2} \left( \frac{c_j}{c \tau D_{ij}} - \frac{c_i}{c \tau D_{0j}} \right) h_i + \sum_{j=0, 1, 2} \left( \frac{c_i}{c \tau D_{ij}} \right) h_j \quad i = 1, 2 \]

(107)

with \( c \tau = c_0 + c_1 + c_2 \). Factors \( D_{ij} \) are termed Maxwell-Stefan diffusivities and the symmetry property \( D_{ij} = D_{ji} \) holds. In equations (107) one notices that the solvent is explicitly involved (the phase termed “zero”) and that only 2 out of 3 equations are linearly independent. In fact, the sum of the three equations lead the null identity, as the left hand side becomes the Gibbs-Duhem equation whereas the right is zero for “zero”). Specialization for the free energy densities of species can still be assumed as in moderately diluted solutions.

Summarizing thus, for diluted solutions assuming the Fickian representation for mass flux (95) and equation (96) as a specialization of mobility tensor, one has

\[ h_{Li+}^m (\phi_{Li+}, \phi^m) = -u_{Li+} c_{Li+} \nabla \left[ \phi_{Li+} \right] \quad x \in V_e \]  

(109)

\[ h_{X}^m (\phi_{X}, \phi^m) = -u_X c_X \nabla \left[ \phi_X \right] \quad x \in V_e \]  

(110)

with \( c_{Li+}^m (\phi_{Li+}, \phi^m) \) and \( c_X^m (\phi_X, \phi^m) \) derived from constitutive identity (105). For concentrated solutions one makes recourse to the theory of Irreversible Thermodynamics, replacing Fickian fluxes \( h_{Li+}^m \) by linear combinations of the gradients of \( Li^+, X^- \) electrochemical potentials as in (106). Equation (105) holds for both species.

1.2 - Constitutive theory for the active particles
Thermodynamics restrictions (18) for active particles suggest that the Li flux $\mathbf{h}_{Li}$ is given by Fick’s law, i.e. a constitutive equations of the form

$$
\mathbf{h}_{Li} = -\mathbf{M}(c_{Li}) \nabla [\mu_{Li}]
$$

with the positive definite tensor $\mathbf{M}(c_{Li})$ termed mobility tensor. Diffusion processes in active particles is thus completely described by the chemical potential $\mu_{Li}$ and its constitutive relationship in terms of the internal energy $u$ (or equivalently the free energy $\psi$)

$$
\mu_{Li} - \rho \frac{\partial u(y)}{\partial c_{Li}} = \mu_{Li} - \rho \frac{\partial \psi(y)}{\partial c_{Li}} = 0
$$

and of the set of variables $y$ that model driving forces. Specific literature in this regard is nowadays broad and several choices for $y$ have been considered.

The deviation from stoichiometry in a solid composition due to atomic diffusion may cause large swelling. If it is not accommodated properly, mechanical stresses arise, which in turn affect intercalation. A classical model that takes volumetric changes into account is the network model of Larche and Cahn [26]. It assumes that the lattice sites of the hosting material form a network within which neutral Lithium can diffuse. The network lattice material, if Si or C for instance, is taken to be insoluble in the electrolyte. Stress dependent families of chemical potential $\mu_{Li}$ have been recently considered by several authors [27, 55, 56, 57, 58, 49] considering large eigenstrain and including non convex double-well potentials to model phase-segregation as well as higher order kinematical descriptors\(^9\).

Here simpler specializations will be considered to the sake of this supplementary material appendix. The Helmholtz free energy density $\psi$ is widely assumed to consist in three separated factors. One, here termed $\psi_{diff}$, describes the pure diffusive process, usually adopting the concentration as the state variable. The second, $\psi_{mech}$, models the elastic energy density, whereas the last one, $\psi_{coupling}$, couples the mechanical and diffusive processes. A classical specialization is the isotropic one that follows

$$
\begin{align*}
\psi_{diff}(c_{Li}) &= \mu_0 c_{Li} + R \Theta \left( c_{Li} \log c_{Li} + \left(c_{Li}^{max} - c_{Li}\right) \log \left( c_{Li}^{max} / c_{Li}\right) \right) \\
\psi_{mech}(\varepsilon) &= \frac{1}{2} \varepsilon \cdot \mathbf{C} \varepsilon = \frac{1}{2} (K \nabla^2 \varepsilon + 2 G \| \mathbf{D} \varepsilon \|)^2 \\
\psi_{coupling}(c_{Li}, \varepsilon) &= -3 K \omega_a c_{Li} \nabla \varepsilon
\end{align*}
$$

with $R$ the universal gas constant and $K$, $G$ are the bulk and shear modulus respectively. Concentration $c_{Li}^{max}$ is reached in the active particles when all accommodating sites are filled, i.e. $c_{Li}^{max}$ is the saturation limit for Lithium in the active particles material. $\omega_a$ is the coefficient of chemical expansion of neutral Lithium in the active host material and $\mu_0$ is a reference value of the chemical potential of the diffusing species. Symbol $\nabla [-]$ denotes the trace operator whereas $\mathbf{D} [-]$ is the deviator operator. Mobility tensor $\mathbf{M}(c_{Li})$ is assumed to be isotropic, in the form

$$
\mathbf{M}(c_a) = M_0 c_{Li} \left( 1 - \frac{c_{Li}}{c_{Li}^{max}} \right) \mathbb{I}
$$

Definition (113) represents the physical requirement that the pure phases $c_{Li} = 0$ and $c_{Li} = c_{Li}^{max}$ have vanishing mobility. The amount $M_0 > 0$ is the mobility constant. Thermodynamics restrictions (18) imply:

$$
\begin{align*}
\sigma &= K \nabla \varepsilon \mathbb{I} + 2 G \mathbf{D} \varepsilon + 3 K \omega_a c_{Li} \mathbb{I} \\
\mu_{Li} &= \mu_0 + R \Theta \log c_{Li}^{max} - R \Theta \log \left( \frac{c_{Li}^{max}}{c_{Li}} - 1 \right) - 3 K \omega_a \nabla \varepsilon
\end{align*}
$$

The latter constitutive equation can be inverted, thus obtaining:

$$
c_{Li} = c_{Li}^{max} \left( 1 + \exp \left[ \frac{\mu_0 + R \Theta \log c_{Li}^{max} - \mu_{Li} - 3 K \omega_a \nabla \varepsilon}{R \Theta} \right] \right)^{-1}
$$

\(^9\)The first order theory adopted in the present work cannot deal with high order material models, which take into account microforces at both scales. To extend the multi scale framework a second order homogenization scheme is required.
that can be seen as a specification for the Grand potential $\Phi$ in thermodynamic restriction (30) for neutral Lithium.

Fick’s law (111) becomes

$$h_{Li}(c_{Li}, \varepsilon) = -D_a \nabla [c_{Li}] + 3 \tilde{D}_a c_{Li} \left( 1 - \frac{c_{Li}}{c_{Li_{\text{max}}}} \right) \nabla [\text{Tr}[\varepsilon]] \quad x \in V_a$$  \hspace{1cm} (117)

with $D_a = M_0 R \vartheta$ the diffusivity coefficient and $\tilde{D}_a = M_0 K_a \omega_a$ a chemical expansion coefficient. In terms of chemical potential, Fick’s law is given in (111) with $c_{Li}$ from (116).

The flow of electrons in the active particles is modeled similarly to the flow of a single charged species in a dilute solution. By defining the Helmholtz free energy as

$$\psi(e, \phi) = \mu^0_e e^{-c_e} + R \vartheta c_e \log c_e + z_e F c_e - \phi$$

it comes out:

$$c_e^{-} (\text{Tr}[\varepsilon], \phi) = \exp \left[ \frac{1}{R \vartheta} (\text{Tr}[\varepsilon] - \mu^0_e - R \vartheta + F \phi) \right]$$  \hspace{1cm} (118)

and finally:

$$h_e^{-} (\text{Tr}[\varepsilon], \phi) = -M (c_e^{-} (\text{Tr}[\varepsilon], \phi)) \nabla [\text{Tr}[\varepsilon]]$$

In terms of concentration and electrical potential, making recourse to equations (95, 96, 99, 100) a Fick’s law of the following kind arises:

$$h_e^{-} (c_e^{-}, \phi) = -u_e^{-} R \vartheta \nabla [c_e^{-}] - z_e^{-} F u_e^{-} c_e^{-} \nabla [\phi]$$  \hspace{1cm} (119)

1.3 - Constitutive theory for the conductive particles

The flow of electrons in conductive particles is modeled as for the active particles, even though electroneutrality conditions are usually respected. No ionic mass transport is present. Conductive particles are generally made of graphite and/or carbon black [47]. Natural and crystalline graphites are known for brittleness. In this regard the classical strain energy function of infinitesimal isotropic elasticity, eventually extended to large deformations in terms of the logarithmic elastic strain, might be the most proper choice.

1.4 - Constitutive theory for electrode foils

In the same spirit of [18] and following Larche and Cahn [59], an homogeneous electrode can be idealized as a network solid. Li will be assumed to form an interstitial solution in this network. Then Lithium may diffuse through the interior of the electrode, driven by variations in concentration or stress according for instance to the isotropic specializations (112). In a half-cell, the electrode can be taken in the form of metallic lithium as in [22], so that no diffusion processes take place as Li is removed/deposited directly from at the electrolyte interface and no current collector is needed. This option is likely more interesting to reproduce experimental setups [5] rather than industrial batteries.

1.5 - Constitutive theory for separators

Not much attention has been put so far to the mechanical constitutive assumptions on the separators. They clearly depend on the manufacture of the separator and its interactions with the electrolyte, that in the current technology of Li-ion batteries [7] might be a solid, a liquid or a gel. This crucial aspect of material modeling falls beyond the scope of the present paper, in which the isotropic linear elastic constitutive law

$$\sigma_e = \lambda_e \text{Tr}[\varepsilon_e] \mathbb{I} + 2 G_e \varepsilon_e$$  \hspace{1cm} (120)

is taken.

1.6 - Constitutive theory for the electric field
The constitutive assumption
\[ e(\eta, \varepsilon, c, \alpha, \sigma, c_{e-}) = u(\eta, \varepsilon, c, \alpha, c_{e-}) + \frac{1}{2\rho} \tau \cdot \tau \] (121)
will be taken. The thermodynamic restriction on the electric field thus becomes
\[ \nabla [\phi] = E \] (122)

Appendix 2 - Microscale governing PDEs

In view of balance equations (54, 55) and of the constitutive assumptions (109, 110), the governing PDEs for mass transport in the electrolyte read:
\[
\begin{align*}
\text{div} \left[ \epsilon^m_{Li} (\overline{\mu}^m_{Li}, \phi^m) \nabla [\overline{c}^m_{Li}] \right] &= 0 & \text{x} \in V_e \\
\text{div} \left[ \epsilon^m_X (\overline{\mu}^m_X, \phi^m) \nabla [\overline{c}^m_X] \right] &= 0 & \text{x} \in V_e 
\end{align*}
\]
Gauss law (58) and the thermodynamic restriction (122) lead to:
\[ \varepsilon_0 \Delta \left[ \phi^m \right] = F (\epsilon^m_{Li} (\overline{\mu}^m_{Li}, \phi^m) - \epsilon^m_X (\overline{\mu}^m_X, \phi^m)) \text{ x} \in V_e \]
In force of the assumption of electrolyte as a perfect fluid, the stress tensor \( \sigma = p \mathbf{I} \) can be evaluated via the momentum balance, that reads:
\[ \nabla [p] + F (\epsilon^m_{Li} - \epsilon^m_X) \nabla [\phi^m] = 0, \quad x \in V_e \] (123)

Gauss law (57) and the thermodynamic restriction (122) lead to:
\[ \varepsilon_0 \Delta \left[ \phi^m \right] = F (\epsilon^m_{Li} - \epsilon^m_X (\overline{\mu}^m_{Li}, \phi^m)) \text{ x} \in V_e \]
whereas current density is governed by
\[ \text{div} \left[ \epsilon^m_{e-} (\overline{\mu}^m_{e-}, \phi^m) \nabla [\overline{\mu}^m_{e-}] \right] = 0 \text{ x} \in V_e \]
Having assumed a linear elastic isotropic constitutive behavior for the conductive particles, balance equation (61) becomes
\[ \lambda_c \nabla \left[ \text{Tr}[\epsilon^m] \right] + 2 G_c \text{div} \left[ \epsilon^m \right] - F (\epsilon^m_{e-} - \epsilon^m_{Li} (\overline{\mu}^m_{Li}, \phi^m)) \nabla [\phi^m] = 0, \quad x \in V_c \]
Force balance equation (61) and mass balance equation (53) become coupled in view of constitutive equations (114), (117):
\[ K_a \nabla \left[ \text{Tr}[\epsilon^m] \right] + 2 G_a \text{div} \left[ \text{Dev}[\epsilon^m] \right] - 3 K_a \omega_a \nabla \left[ \epsilon^m_{Li} \right] - F (\epsilon^m_{e-} - \epsilon^m_{Li}) \nabla [\phi^m] = 0 \text{ x} \in V_a \] (124)
\[ -D_a \Delta \left[ \epsilon^m_{Li} \right] + 3 \tilde{D}_a (1 - 2 \frac{\epsilon^m_{Li}}{\epsilon^m_{Li}}) \nabla \left[ \epsilon^m_{Li} \right] \cdot \nabla \left[ \text{Tr}[\epsilon^m] \right] + 3 \tilde{D}_a (1 - \frac{\epsilon^m_{Li}}{\epsilon_{Li}^{max}}) \epsilon^m_{Li} \Delta \left[ \text{Tr}[\epsilon^m] \right] = 0 \text{ x} \in V_a \] (125)
Equations (124), (125) are stated in terms of electrochemical potentials \( \overline{\mu}_{e-}, \mu_{Li} \) in view of equations (116), (118). Gauss law (57) and the thermodynamic restriction (122) lead to:
\[ \varepsilon_0 \Delta \left[ \phi^m \right] = F (\epsilon^m_{e-} - \epsilon^m_{Li} (\overline{\mu}^m_{Li}, \phi^m)) \text{ x} \in V_a \] (126)
whereas current density is governed by
\[ \text{div} \left[ \epsilon^m_{e-} (\overline{\mu}^m_{e-}, \phi^m) \nabla [\overline{\mu}^m_{e-}] \right] = 0 \text{ x} \in V_a \] (127)
Appendix 3 - The electroneutrality assumption

Electroneutrality

\[ \sum_\alpha z_\alpha c_\alpha = 0 \] (128)

is often assumed in the electrolyte and in electrodes [24]. For the solution of binary salt LiX object of study it holds

\[ c_{\text{Li}^+} = c_{\text{X}^-} = 0 \] (129)

In this appendix the impact and the applicability of electroneutrality assumption will be analyzed.

3.1 - Range of validity

The electrochemical part of the problem in the electrolyte is formulated in terms of three potentials \( \mu_{\text{Li}^+}, \mu_{\text{X}^-}, \phi \) and the balance laws of mass and Gauss law properly describe their evolution. May electroneutrality over constrain the problem?

To investigate this issue, electroneutrality will be assumed and its impact evaluated in the framework of diluted electrolyte solutions. Gauss law reads:

\[ \text{div} [\mathbf{E}] = \frac{F}{\varepsilon_0} (c_{\text{Li}^+} - c_{\text{X}^-}) = 0 \]

and by means of thermodynamic restriction (27)

\[ \Delta [\phi^m] = 0 \quad x \in V_e \] (130)

The conservation of charge in the electrolyte is linearly dependent upon equations (54) and (55) in view of electroneutrality and mass balances:

\[ \text{div} [\mathbf{i}^m_e] = 0 \quad x \in V_e \] (131)

Owing to Fick’s law (101), the flux of Li-ions is constitutively linked to concentration and electrostatic potential. Applying Faraday’s law (3) and electroneutrality condition (129), the current density constitutive equation follows:

\[ \mathbf{i}^m_e = -l_e \nabla [c^m_{\text{Li}^+}] - \kappa^m_e \nabla [\phi^m] \quad x \in V_e \] (132)

having set: \( \kappa_e = F^2 (u_{\text{Li}^+} + u_{\text{X}^-}) c^m_{\text{Li}^+}, l_e = F (D_{\text{Li}^+} - D_{\text{X}^-}), \) and \( D_{\text{X}^-} = u_{\text{X}^-} R \vartheta \). Parameter \( \kappa_e \) is termed conductivity of the solution.

Furthermore, by substitution of (101) into a linear combination of mass balance equations (54-55) the strong form of the steady-state problem of ion-transport reads:

\[ \Delta [c^m_{\text{Li}^+}] = 0 \quad x \in V_e \] (133)

Inserting (132) into (131), the requirement:

\[ \nabla [c^m_{\text{Li}^+}] \cdot \nabla [\phi^m] = 0 \quad x \in V_e \] (134)

comes out in view of (130) and (133). Such an identity is usually not satisfied, because \( \nabla [c^m_{\text{Li}^+}] \) is neither vanishing nor orthogonal to the electric field. However, the effect of charge on electrochemical potential is hugely greater than the effect of concentration: this predominance of migration with respect to diffusion justifies electroneutrality assumption in the presence of an electric field across the battery cell, at least away from the Stern and Gouey-Chapman layers.

Once the steady state is reached in the electrolyte, if the mass flux of anions is zero the requirement (134) becomes

\[ \nabla [\phi^m] \cdot \nabla [\phi^m] = 0 \quad x \in V_e \] (135)

thus requiring a small variation of the electrostatic potential in the bulk.
3.2 - Constitutive theory

In view of Fick’s law (101), Faraday’s law (3) and electroneutrality (128), for the binary salt at hand one has:

\[
i = \sum_{\alpha=1}^{2} z_\alpha F h_\alpha = - \sum_{\alpha=1}^{2} z_\alpha F D_\alpha \nabla [c_{Li^+}] - \sum_{\alpha=1}^{2} z_\alpha^2 F^2 u_\alpha c_{Li^+} \nabla [\phi]
\]  
(136)
in the absence of gradients of concentration (and thus of chemical potential in view of (99)) current is driven by migration only and it holds:

\[
i = - \sum_{\alpha=1}^{2} z_\alpha^2 F^2 u_\alpha c_{Li^+} \nabla [\phi] = \kappa_e \nabla [\phi]
\]  
(137)
i.e. Ohm’s law with \(\kappa_e\) termed electrolytic conductance. Linearity of \(\kappa_e\) with respect to concentration has been experimentally assessed at concentrations far from the saturation limit in several binary salt solutions.

3.3 - A property of binary electrolyte.

For the binary salt LiX under consideration, and defining terms by comparison with (103), one writes:

\[
\overline{\mu}_{Li^+} = \mu_{Li^+}^0 (f_{Li^+,f_{X^-}}) + R \vartheta \log c_{Li^+} + F\phi
\]
\[
\overline{\mu}_{X^-} = \mu_{X^-}^0 (f_{Li^+,f_{X^-}}) + R \vartheta \log c_{X^-} - F\phi
\]

and by subtraction

\[
\phi(\overline{\mu}_{Li^+},\overline{\mu}_{X^-}) = \frac{\overline{\mu}_{Li^+} - \overline{\mu}_{X^-} - \mu_{Li^+}^0 (f_{Li^+,f_{X^-}}) + \mu_{X^-}^0 (f_{Li^+,f_{X^-}})}{2F}
\]  
(138)
in view of electroneutrality. In view of property (138) the electric state of the electrolyte can be expressed in terms of the electrochemical potential of the two ions in the solution. The concentration of Li-ions can be thus written as:

\[
c_{Li^+}(\overline{\mu}_{Li^+},\overline{\mu}_{X^-}) = \exp \frac{3\overline{\mu}_{Li^+} - \overline{\mu}_{X^-} - 3\mu_{Li^+}^0 (f_{Li^+,f_{X^-}}) + \mu_{X^-}^0 (f_{Li^+,f_{X^-}})}{2R \vartheta}
\]  
(139)
in the same terms. By comparison with (105) it can be observed that in view of electroneutrality \(c_{Li^+}\) becomes independent on \(\phi\).

3.4 - Two scale formulation

3.4.1 - Macroscale

The conservation of charge in the electrolyte under the assumption of electroneutrality is provided by the linear combination of equations (38) and (39) for anions and cations.

\[
\text{div} \left[ \mathbf{1}_e^M \right] = -F h_{Li^-} \quad \mathbf{x} \in \Omega_{Ca} \times [0,T]
\]  
(140)

In view of the assumption of electroneutrality Gauss laws become homogeneous and only one macroscopic electric field \(\mathbf{E}\) suffices. Similarly, as the electrostatic forces of interaction \(\mathbf{b}_\zeta\) vanishes, one single stress field only is required in (44-46).

3.4.2 - Microscale

Body forces \(\mathbf{b}_\zeta\) are insignificant as far as the electrode and electrolyte are concerned if they remain electrically neutral. Inertia effects as well as bulk forces are neglected too, so that the force balance (5) specializes as:

\[
\text{div} \left[ \mathbf{\sigma}^m \right] = 0 \quad \mathbf{x} \in V
\]  
(141)
Constitutive theories for the mass transport can be expressed in terms of electrochemical potentials, particularizing appendix 0. For *diluted solutions*, assuming the Fickian representation for mass flux (95) and equation (96) as a specialization of mobility tensor $\mathbf{M}(\kappa_e)$, one has

$$h^{m}_{Li^+}(\mathbf{p}_{Li^+}, \mathbf{p}_{X^-}) = -u_{Li^+} e^{m}_{Li^+} \nabla \phi$$  \hspace{0.5cm} x \in V_e \hspace{1cm} (143)$$

$$h^{m}_{X^-}(\mathbf{p}_{Li^+}, \mathbf{p}_{X^-}) = -u_{X^-} c^{m}_{X^-} \nabla \phi$$  \hspace{0.5cm} x \in V_e \hspace{1cm} (144)$$

with $c^{m}_{Li^+} = c^{m}_{X^-}$ derived from constitutive identity (139) in terms of the two distinct electrochemical potentials. For *concentrated solutions* one makes recourse to the theory of Irreversible Thermodynamics, replacing Fickian fluxes (143–144) by linear combinations of the gradients of $Li^+$, $X^-$ electrochemical potentials as in (106). Again electroneutrality allows to take advantage of (139) for both species.

In terms of concentrations, constitutive theories read as follows. For *infinitely diluted solutions* one considers Fick’s law (101) together with (132). In the absence of concentration gradients, one defines

$$i^{m}_{Li^+} = -F^2 u_{Li^+} e^{m}_{Li^+} \nabla \phi = \frac{u_{Li^+}}{u_{Li^+} + u_{X^-}} i^{m} = t_{Li^+} i^{m} , \hspace{0.5cm} x \in V_e$$ \hspace{1cm} (145)$$

An analogous equation applies for $i^{m}_{X^-}$. Parameter $t_{Li^+} = u_{Li^+} (u_{Li^+} + u_{X^-})^{-1}$ is thus a material property for the salt in the solution. It is termed *transference number* or *transport number*. It must be stressed that equation (145) holds in the absence of concentration gradients only. In such a case, constitutive equation (101) can be rewritten rigorously as:

$$h^{m}_{Li^+}(c^{m}_{Li^+}, \phi) = -D_{Li^+} \nabla \left[ c^{m}_{Li^+} \right] - \frac{t_{Li^+}}{F} i^{m}_{Li^+} , \hspace{0.5cm} x \in V_e$$ \hspace{1cm} (146)$$

For *concentrated solutions* one should make recourse to the theory of Irreversible Thermodynamics, replacing Fickian flux (101) by linear combinations of the gradients of all involved electrochemical potentials as in (106). To have again the mass flux of each phase to be constitutively independent on the electrochemical potential of other phases, the notion of transference number has been used by Newman - see [24], chapter 12 - also in the case of concentrated solutions:

$$h^{m}_{Li^+}(c^{m}_{Li^+}, \phi) = -D_c(c^{m}_{Li^+}) \nabla \left[ c^{m}_{Li^+} \right] - \frac{t_{Li^+}(c^{m}_{Li^+})}{F} i^{m}_{Li^+} , \hspace{0.5cm} x \in V_e$$ \hspace{1cm} (147)$$

Parameter $D_c$ represents the *usually measured* diffusion coefficient of the binary salt which is not provided by the Nernst-Einstein equation anymore. It is related to the diffusion coefficient of the electrolyte by an activity coefficient (see [24], chapter 12 formula (12.12) or [22], formula (2)) thus becoming a function of concentration $c_{Li^+}$. Furthermore, the transference number $t_{Li^+}(c_{Li^+})$ has now to be taken as an unknown function. It is no longer a material property and it depends upon concentration. It is a measurable quantity however, and outcomes from tailored experiments that provided accurate estimation of $t_{Li^+}(c_{Li^+})$ resulted in an abundant and still increasing scientific literature.

The current density $i^{m}_{Li^+}$ was derived in [24] as a function of the *usually measured* conductivity of the solution, here again denoted with $\kappa_e$ with a small abuse of notation\(^\text{10}\), and of the *reference electrode potential* $\phi$ with respect to an actual electrode, usually a Lithium reference electrode.

$$i_e(c^{m}_{Li^+}, \phi) = -\kappa_e \nabla \phi - \chi_e(c^{m}_{Li^+}) \nabla \phi$$  \hspace{0.5cm} x \in V_e \hspace{1cm} (148)$$

with

$$\chi_e(c^{m}_{Li^+}) = -2 R \vartheta \frac{F}{u_{Li^+} + u_{X^-}} \left( 1 + \frac{\partial \log f_+}{\partial \log c^{m}_{Li^+}} \right) \left( 1 - t_{Li^+}(c^{m}_{Li^+}) \right)$$ \hspace{1cm} (149)$$

The flow of electrons in the active particles is modeled similarly to the flow of a single charged species in a dilute solution. The assumption will be made that in steady state conditions charge transport in the

\(^\text{10}\) In fact it does not coincide with the one for ideal solutions and it depends upon the concentration $c^{m}_{Li^+}$.
active particles involves electrons only, whereas the flux of positive charges is null at all \(x \in V_a\). By such an assumption and electroneutrality from the counterpart of (119) it comes out:

\[
R \partial \rho \frac{1}{c_v} \nabla [c_{v-}] = -F \nabla [\phi] \tag{150}
\]

and

\[
h_{c-} = 2F u_{c-} c_{v-} \nabla [\phi] \tag{151}
\]

Constitutive law (118) applies. As charge movement is due to electron flux \(h_{c-}\) only, the current density amounts at \(i_{c-}^m = -F h_{c-}\) and Ohm’s law relates current density to the electric potential:

\[
i_{c-}^m = -\kappa_a \nabla [\phi^m] \quad x \in V_a \tag{152}
\]

with \(\kappa_a = 2F^2 u_{c-} c_{v-}\). A similar outcome applies to conductive particles.

By substitution of (101) into the mass balance (54) and of (132) into charge balance (131) the strong form of the steady-state problem of ion-transport in the electrolyte comes out in the assumptions of electroneutrality and dilute solutions:

\[
\Delta [c_{Li,+}^m] = 0, \quad x \in V_e \tag{153}
\]

\[
\kappa_e^m \Delta [\phi^m] + \nabla [\kappa_e^m] \cdot \nabla [\phi^m] = 0, \quad x \in V_e \tag{154}
\]

Equation (153) comes out after inserting (101) for anions \(X^-\) into the mass balance (55) and subtracting. Equation (153) is in terms of \(c_{Li,+}^m\) and the system of differential equations becomes uncoupled.

By substitution of (147) into the mass balance (54) and of (148) into charge balance (131) the strong form of the problem of ion-transport in the electrolyte comes out in the assumptions of electroneutrality and concentrated solutions:

\[
-D_e \Delta [c_{Li,+}^m] - \nabla [D_e] \cdot \nabla [c_{Li,+}^m] + \frac{1}{F} (\kappa_e \nabla [\phi^m] + \chi_e \nabla [c_{Li,+}^m]) \cdot \nabla [t_{Li,+}(c_{Li,+}^m)] = 0, \quad x \in V_e \tag{135}
\]

\[
\chi_e^m \Delta [c_{Li,+}^m] + \kappa_e^m \Delta [\phi^m] + \nabla [\kappa_e^m] \cdot \nabla [\phi^m] + \nabla [\chi_e^m] \cdot \nabla [c_{Li,+}^m] = 0, \quad x \in V_e \tag{156}
\]

with \(\chi_e^m\) as in equation (149). Balance of mass is equivalent to equation (153) if \(D_e\) and \(t_{Li,+}(c_{Li,+}^m)\) are constant in the solution, as in case of diluted solutions. Assuming that those two parameters are constant is a strong statement that however simplifies the formulation of the governing PDEs significantly. In such a case, equation (156) reduces to (154) in view of the definition of \(\chi_e^m\).

The governing PDEs can be written in terms of the electrochemical potentials \(\mu_{Li,+}^m, \mu_{X^-}^m\) rather than concentration \(c_{Li,+}^m\) and \(\phi\) by exploiting identities (138-139) into (153-156).

The current density in the conductive particles is related to the electric potential by the classical Ohm’s law (152) with \(\kappa_c\) in place of \(\kappa_a\). Conservation of charge and mass (56) lead to

\[
\Delta [c_{c-}^m] = 0 \quad x \in V_c \tag{157}
\]

\[
\kappa_c^m \Delta [\phi^m] + \nabla [\kappa_c^m] \cdot \nabla [\phi^m] = 0 \quad x \in V_c \tag{158}
\]

These equations are uncoupled to the balance equation (141), that in view of linear isotropic elasticity assumption becomes

\[
\lambda_c \nabla [\text{Tr}[\varepsilon]] + 2G_c \text{div} [\varepsilon] = 0 \quad x \in V_c \tag{159}
\]

Analogously, conservation of charge and mass (56) lead to

\[
\Delta [c_{c-}^m] = 0 \quad x \in V_a \tag{160}
\]

\[
\kappa_a^m \Delta [\phi^m] + \nabla [\kappa_a^m] \cdot \nabla [\phi^m] = 0 \quad x \in V_a \tag{161}
\]