



Thermodynamic consistent transport theory of Li-ion batteries

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ABSTRACT

Most Li ion insertion batteries consist of a porous cathode, a separator filled with electrolyte and an anode, which very often also has some porous structure. The solid part especially in the cathode is usually produced by mixing a powder of the actual active particles, in which Li ions will be intercalated, binder and carbon black to enhance the electronic conductivity of the electrode. As a result the porous structure of the electrodes is very complex, leading to complex potential, ion and temperature distributions within the electrodes. The intercalation and deintercalation of ions cannot be expected to be homogeneously distributed over the electrode due to the different transport properties of electrolyte and active particles in the electrode and the complex three-dimensional pore structure of the electrode. The influence of the final microstructure on the distribution of temperature, electric potential and ions within the electrodes is not known in detail, but may influence strongly the onset of degradation mechanisms. For being able to numerically simulate the transport phenomena, the equations and interface conditions for ion, charge and heat transport within the complex structure of the electrodes and through the electrolyte filled separator are needed. We will present a rigorous derivation of these equations based exclusively on general principles of nonequilibrium thermodynamics. The theory is thermodynamically consistent i.e. it guarantees strictly positive entropy production. The irreversible and reversible sources of heat are derived within the theory. Especially the various contribution to the Peltier heat due to the intercalation of ions are obtained as a result of the theory.

Research highlights: ► Thermodynamic consistent transport theory for Li ion batteries ► Derivation of all irreversible and reversible heat sources in Li ion batteries ► Closed set of equations for ion, charge and heat transport in Li ion batteries ► Theory of Peltier heat for Li ion intercalation ► Microstructure resolved transport in porous electrodes

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1. Introduction

Understanding the heat generation and temperature distribution in Li ion battery cells is of great practical interest. Many degradation processes in Li ion batteries are caused by and most of them are enhanced under temperature increase [1,2]. Thermal runaway may begin as a very local phenomenon by initiating an exothermal reaction at a local hotspot. Therefore the average temperature of a cell is not sufficient to determine the beginning of a thermal runaway. A spatially resolved mathematical description of the processes on the scale of the cell would allow to simulate the behavior of the cell under varying operating conditions and to detect the probability of dangerous hotspots.

Mathematical modeling of Li-ion batteries on cell resolved level was pioneered by the work of Newman and his coworkers [3–5] and extended and refined by many other authors [6–8]. The modeling approaches are based on transport equations for Li ions and

charges in the electrolyte as well as in the active particles of cathode and anode under isothermal conditions. Most modeling approaches for the thermal behavior of batteries are concentrating on overall thermal balance equations for a whole cell [9–14] by combining phenomenologically thermodynamic considerations on entropy or enthalpy changes within a cell with reasonable assumptions on out of equilibrium processes like Joule heating, heat of mixing, Peltier effect and Soret effect. An approach based on local continuity equations for the temperature was presented in [15], extending previous work on species and charge transport in batteries [16]. These authors focused on deriving macroscopic equations for the heat transport in porous electrodes using the volume averaging technique. The microscopic equation for the temperature was formulated without considering possible changes of the transport equations describing species and charge transport. Also the interface conditions have not been derived. Fully coupled models have been considered for battery stacks [17] and other types of batteries (see e.g. [18,19]). Also in these cases the equations were not derived but formulated as balance equations in which known physical effects as well as the reaction kinetics for all relevant chemical reactions were phenomenologically incorporated.

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A different approach to treat transport in electrochemical systems is the systematic approach of nonequilibrium thermodynamics [20] pioneered by Landau [21,22]. In this approach only conservation equations and general principles of statistical mechanics were used to derive the general form of the relevant transport equations. Only measurable quantities like thermodynamic derivatives and transport coefficients enter the equations. The Onsager relations which guarantee the positivity of the entropy production and impose strict relations between the equations for densities, charges and temperature, play a central part in the derivation. Chemical reactions can easily be treated within this formalism [20]. The interface conditions can also be derived by necessary continuity constraints (as e.g. conservation of charges, energy, etc.) and considering the physical and chemical processes within the interface [20]. Contrary to the phenomenological approaches the terms contributing to the heat production are systematically derived using nothing else but generally valid thermodynamic relations and total energy conservation, instead of just physical intuition and experimental experience. In this manner it is made certain that no source of heat is neglected, if all hydrodynamic variables and all relevant chemical reactions are taken into account.

An especially elegant form of this formalism was recently used to derive a hydrodynamic theory of electromagnetic field in continuous media [23–26], which can also be applied to charged and magnetic liquids [27]. Also charge and species transport in Li ion batteries can be dealt with using the nonequilibrium thermodynamics framework [28]. We will derive in the following the complete set of equations including all interface conditions for the ion, charge and thermal transport in Li ion battery cells. We will consider a spatial scale L which is large compared to the scale L_{DL} of the diffuse double layer (i.e. $L \gg L_{DL} \sim 10\text{--}20\text{ nm}$ [4]). Concentrated electrolytes are neutral on this scale due to the strong Coulomb interactions between the ions leading to an extremely small Debye screening length. Only in the double layer around the active particle, which usually have diameters on micrometer scale, potential gradients are strong enough to cause charge separation [4]. Also active particles fulfill charge neutrality although the mechanism for obtaining charge neutrality is very different. In active particles it is the large mobility of electrons which guarantees charge neutrality. The charge of an inserted Li ion is instantaneously shielded by local rearrangements of electronic charges and the transport of electrons into the active particles over the current collectors. In the electrolyte charge neutrality will lead to highly correlated motion of negative and positive ions. We will make explicit use of charge neutrality in the derivation of our equations.

In addition to naturally reducing the numbers of relevant equations, the use of charge neutrality also guarantees, that the transport coefficients appearing in theory are the measurable quantities of the electrolyte. Let us for example consider the diffusion processes in a molten salt consisting of positive and negative ions. In general the self-diffusion coefficients are different for the two kinds of ions. If there were no interaction between the ions, we could expect to obtain free electric charges in relaxation processes even if the initial perturbation were neutral due to the different diffusion length of the ions. In reality the strong Coulomb interaction between the ions prevents the appearance of free charges. The process relevant for diffusion is in fact the collective interdiffusion process with a uniquely defined interdiffusion coefficient for both species. This unique quantity for positive and negative ions will appear naturally in our theory.

To derive the transport equations in the electrolyte and the solid particles we use a general and rigorous theory for polarizable, conducting media introduced in [23] and generalized in [24]. The theory is based on general thermodynamic principles, Maxwells theory for electromagnetic fields and Onsagers reciprocal relations.

Although transport mechanisms in active particles and electrolyte can be very different on the microscopic (atomic) scale, their macroscopic form just differ in the functional dependencies and the size of the transport coefficients. For example in active particles charge is transported mainly by pure electronic conduction. The contribution of the ion diffusion in the active particles to the electric current can be neglected due to the large mobility of the electrons compared to the ions. Charge transport in the electrolyte on the other side is exclusively due to ionic transport. In fact the transfer of electrons into the electrolyte would result in the reduction of Li ions in the electrolyte to metallic lithium and is considered to be one of the many degradation mechanisms in Li ion batteries [1]. Macroscopically, the differences in the microscopic charge transport mechanisms are reflected in different functional dependencies of the charge conductivity coefficients on temperature and Li ion concentration. The ionic conductivity in the electrolyte is usually strongly dependent on the concentration of Li ions. The electronic conductivity of the active particles is basically not affected by it and can be assumed to constant. In addition, the transference number of ions in active particles is approximately zero due to the vanishing contribution of ion diffusion to the electrical current.

2. Model

Originally the theory of Henjes and Liu [23] was used to derive the hydrodynamic equations for a one component polarizable liquids. But the principles can easily be applied to a mixture of a dissociating salt and a solvent i.e. for a generic electrolyte as used in batteries. The reduction to the transport in the solid particle is straight forward after the full set of equations for the electrolyte are derived. Although we have to deal with a at least three component system of positive and negative ions as well as neutral solvent molecules, the problem can be reduced to an effective one component problem using two constraints, which are applicable to the physical situation of a concentrated electrolyte in a battery. The first observation is that convective transport is highly unlikely under normal operating conditions in a battery. We therefore may safely assume that the center of mass of any hydrodynamic volume element is at rest. This assumption allows to eliminate the concentration of the neutral solvent as independent variable. With M_0 , M_+ , M_- being the molar masses of solvent and positive and negative ions respectively we get in the absence of convection the relations:

$$M_0 dc_0 + M_+ dc_+ + M_- dc_- = 0 \quad (1)$$

for the changes in the respective concentrations.

The second observation concerns the occurrence of finite *free* charges in a volume element. It can easily be estimated [4] that the electric fields which where necessary to impose charge separation on a micrometer scale are much bigger than the average fields present in a battery. Charge separation is only observed in the double layer around active particles on a scale of the order of 10–20 nm. The present theory will be restricted to scales above 100 nm. A detailed theory for the linear and nonlinear phenomena in the double layer can be found in [29,30]. If we denote molar concentrations of positive and negative ions of charge z_+ and z_- with c_+ and c_- , respectively, charge neutrality requires

$$\nu_+ z_+ c_+ + \nu_- z_- c_- = 0 \quad (2)$$

where ν_+ , ν_- are the stoichiometric numbers of positive and negative charges. It is therefore sufficient to determine the transport equations for the concentration $c = c_+ = -(\nu_- z_- / \nu_+ z_+) c_-$. For notational simplicity we restrict our theory to a binary salt with $\nu_+ = \nu_- = 1$ and consequently $z_- = -z_+$ as well as

$$c_+ = c_- \quad (3)$$

The fundamental thermodynamic relation for a polarizable system in an external electromagnetic field is given by [23]

$$de = Tds + \mu_+ dc_+ + \mu_- dc_- + \mu_0 dc_0 + \vec{E} \cdot d\vec{D} + \vec{H} \cdot d\vec{B} \quad (4)$$

Here e , s , μ_i are the energy density, entropy density and the chemical potential of species i . \vec{E} , \vec{D} , \vec{B} , \vec{H} are electric field, electric displacement, magnetic induction and magnetic field, respectively. Using (1) and (3), Eq. (4) reduces to

$$de = Tds + \mu dc + \vec{E} \cdot d\vec{D} + \vec{H} \cdot d\vec{B} \quad (5)$$

where $c \equiv c_+$ is the concentration of Li-ions and the effective chemical potential μ of the lithium ions is given by

$$\mu = \mu_+ - \frac{M_+}{M_0} \mu_0 - \frac{z_-}{z_+} \left(\mu_- - \frac{M_-}{M_0} \mu_0 \right) \quad (6)$$

For a binary charge neutral salt this reduces to

$$\mu = \mu_+ + \mu_- - \frac{M_- + M_+}{M_0} \mu_0 \quad (7)$$

The next building blocks are the conservation equation for concentration of Li ion, charge density ρ_{el} , entropy as well as the Maxwell equations. Note that the macroscopic velocity is set to zero, due to the main assumption of convection free transport in Li ion batteries. The equation for ρ_{el} is obtained from the conservation equations of ions:

$$\frac{\partial c_+}{\partial t} = -\vec{\nabla} \cdot \vec{N}_+ \quad (8)$$

$$\frac{\partial c_-}{\partial t} = -\vec{\nabla} \cdot \vec{N}_- \quad (9)$$

Here \vec{N}_+ , \vec{N}_- are the fluxes (i.e. the number of moles per unit time and unit area) of the positive Li ions and the negative counter ions, respectively. Using (3) we obtain with $\rho_{el} = z_+ c_+ + z_- c_-$ and the definition of the electric current $\vec{j} = z_+ \vec{N}_+ + z_- \vec{N}_-$:

$$\frac{\partial \rho_{el}}{\partial t} = 0 = -\vec{\nabla} \cdot \vec{j} \quad (10)$$

From the Maxwell equation follows:

$$\vec{E} \cdot \partial_t \vec{D} + \vec{H} \cdot \partial_t \vec{B} = -\vec{\nabla} \cdot (\vec{E} \times \vec{H}) - \vec{j} \cdot \vec{E} \quad (11)$$

The general form of the entropy equation is given by

$$\partial_t s = -\vec{\nabla} \cdot \left(\frac{\vec{q}}{T} \right) + \frac{R}{T} \quad (12)$$

Here \vec{q} is the heat flux. The entropy production R can be derived by combining the first law (5) and the conservation of the total energy. From the first law (5) we obtain:

$$\partial_t e = T \partial_t s + \mu \partial_t c + \vec{E} \cdot \partial_t \vec{D} + \vec{H} \cdot \partial_t \vec{B} \quad (13)$$

With (8), (11) and (12), Eq. (13) transforms into

$$\partial_t e = -\vec{\nabla} \cdot (\vec{q} + \vec{N}_+ \mu + \vec{E} \times \vec{H}) + R + \vec{q} \cdot \frac{\vec{\nabla} T}{T} - \vec{j} \cdot \vec{E} + \vec{N}_+ \cdot \vec{\nabla} \mu \quad (14)$$

Due to the conservation of total energy the change in the local energy has to fulfill a continuity equation i.e.:

$$\partial_t e = -\vec{\nabla} \cdot \vec{J}_e \quad (15)$$

By comparing (14) and (15) we obtain the entropy production R as

$$R = -\vec{q} \cdot \frac{\vec{\nabla} T}{T} - \vec{N}_+ \cdot \vec{\nabla} \mu + \vec{j} \cdot \vec{E} \quad (16)$$

The entropy production has to be strictly positive or zero. This requirement imposes strong constraints on the constitutive relations for the fluxes \vec{q} , \vec{N}_+ and \vec{j} . Since the chemical potential is

difficult to measure it is more convenient to work with c , T and \vec{E} as independent variable. We therefore rewrite Eq. (16) as

$$R = -\vec{Q} \cdot \frac{\vec{\nabla} T}{T} - \left(\frac{\partial \mu}{\partial c} \right) \vec{N}_+ \cdot \vec{\nabla} c + \vec{j} \cdot \vec{E} \quad (17)$$

with $\vec{Q} = \vec{q} + \vec{N}_+ T (\partial \mu / \partial T)$. The expression for the entropy production defines the independent thermodynamic fluxes \vec{Q}/T , $(\partial \mu / \partial c) \vec{N}_+$ and \vec{j} , for which constitutive equations have to be formulated. In order to guarantee positiveness of the entropy production R , the constitutive equations have to be chosen such, that the expression for R (17) is a positive definite binary form. The most general expression for the fluxes is therefore given by

$$\begin{pmatrix} -\left(\frac{\partial \mu}{\partial c}\right) \vec{N}_+ \\ \vec{j} \\ -\frac{\vec{Q}}{T} \end{pmatrix} = \begin{pmatrix} \left(\frac{\partial \mu}{\partial c}\right) \alpha & -\left(\frac{\partial \mu}{\partial c}\right) \frac{\kappa t_+}{F z_+} & \left(\frac{\partial \mu}{\partial c}\right) \nu \\ -\left(\frac{\partial \mu}{\partial c}\right) \frac{\kappa t_+}{F z_+} & \kappa & -\beta \kappa \\ \left(\frac{\partial \mu}{\partial c}\right) \nu & -\beta \kappa & \frac{\gamma}{T} \end{pmatrix} \times \begin{pmatrix} \vec{\nabla} c \\ \vec{E} \\ \vec{\nabla} T \end{pmatrix} \quad (18)$$

The symmetry of the Onsager matrix in Eq. (18) is necessary for the positiveness of the entropy production and a consequence of fundamental principles of nature [20]. The physical meaning of the various transport coefficients α , κ , γ , β , ν , t_+ is getting more obvious after transforming equivalently the constitutive equations into the more traditional form:

$$\vec{N}_+ = -D \vec{\nabla} c + \frac{t_+}{z_+ F} \vec{j} - \frac{D c k_T}{T} \vec{\nabla} T \quad (19)$$

$$\vec{j} = \kappa \vec{E} - \kappa \frac{t_+}{z_+ F} \left(\frac{\partial \mu}{\partial c} \right) \vec{\nabla} c - \beta \kappa \vec{\nabla} T \quad (20)$$

$$\vec{Q} = -\lambda \vec{\nabla} T + \beta T \vec{j} + k_T c \left(\frac{\partial \mu}{\partial c} \right) \left(\vec{N}_+ - \frac{t_+}{z_+ F} \vec{j} \right) \quad (21)$$

In this form the entropy production has the simple form:

$$R = \lambda \frac{(\vec{\nabla} T)^2}{T} + \frac{\vec{j}^2}{\kappa} + \left(\frac{\partial \mu}{\partial c} \right) \frac{(\vec{N}_+ - (t_+/z_+ F) \vec{j})^2}{D} \quad (22)$$

In order to be positive each term in the expression (22) has to be positive i.e. the heat conductivity λ , the electric conductivity κ and the interdiffusion coefficient D have to be positive.

Eq. (20) can also be expressed using the electrochemical potential $\varphi = \mu / (z_+ F) + \Phi$, where Φ is defined by $\vec{E} = -\vec{\nabla} \Phi$:

$$\vec{j} = -\kappa \vec{\nabla} \varphi - \kappa \frac{t_+ - 1}{z_+ F} \left(\frac{\partial \mu}{\partial c} \right) \vec{\nabla} c - \left(\beta - \frac{1}{z_+ F} \left(\frac{\partial \mu}{\partial T} \right) \right) \kappa \vec{\nabla} T \quad (23)$$

The electric conductivity κ in the electrolyte is a pure ionic conductivity. In addition to the ionic conductivity, the transference number t_+ of Li ions and the Seebeck coefficient β are the relevant transport coefficients for the electric current. The transference number also appears in the relation for the ionic flux \vec{N}_+ and determines the amount of ion flux contributed by the electric current. The Seebeck coefficient has the units VK^{-1} and is related to the Peltier coefficient Π by $\Pi = T\beta$. It quantifies the thermoelectric effect in the electrolyte or the active particles. The Seebeck coefficient can in principle be positive or negative.

The two additional transport coefficients relevant for the ionic flux are the inter diffusion coefficient D and the Soret coefficient k_T . The interdiffusion coefficient D , appearing in the relation for the

ionic flux \vec{N}_+ , is measured in the limit of zero electrical current and zero temperature gradient. It is given by

$$D = \alpha - \left(\frac{\partial \mu}{\partial c} \right) \kappa \left(\frac{t_+}{Fz_+} \right)^2 \quad (24)$$

Since D has to be positive the Onsager coefficient α and the transference number fulfill an obvious inequality relation. The Soret coefficient k_T quantifies thermodiffusional processes and is given by

$$\frac{D c k_T}{T} = \nu - \kappa \frac{\beta t_+}{Fz_+} \quad (25)$$

Usually the Soret coefficient is of order 0.6–1.5 [31], but the overall size of the Soret effect is believed to be very small in liquids and electrolytes [32]. Therefore the ion flux induced by temperature gradients is neglected compared to the one caused by electric currents and gradients in concentrations.

The last transport coefficient is the thermal conductivity λ measured in the limit of vanishing electric current and vanishing ionic flux. It is given by

$$\lambda = \gamma - \left(\frac{\partial \mu}{\partial c} \right) \frac{D}{T} (k_T c)^2 - \kappa T \beta^2 \quad (26)$$

It also has to be strictly positive in order to guarantee positive entropy production R .

2.1. Heat transport

The equation for the temperature can be derived from the entropy balance (12) and the expression for the entropy production (17) and the relation:

$$T \partial_t s = c_p \rho \partial_t T + T \left. \frac{\partial s}{\partial c} \right|_T \partial_t c \quad (27)$$

where c_p and ρ are the specific heat per unit mass and the mass density of the electrolyte or the active particles. Using the thermodynamic relation $(\partial s / \partial c)|_T = -(\partial \mu / \partial T)|_c$ and the continuity Eq. (8) we obtain:

$$c_p \rho \partial_t T = -\vec{\nabla} \cdot \vec{q} - \vec{N}_+ \cdot \vec{\nabla} \mu + \vec{j} \cdot \vec{E} - T \left(\frac{\partial \mu}{\partial T} \right) \vec{\nabla} \cdot \vec{N}_+ \quad (28)$$

Transforming from the original heat flux \vec{q} to the renormalized heat flux \vec{Q} we get

$$c_p \rho \partial_t T = -\vec{\nabla} \cdot \left(\vec{Q} - T \vec{N}_+ \left(\frac{\partial \mu}{\partial T} \right) \right) - \left(\frac{\partial \mu}{\partial c} \right) \vec{N}_+ \cdot \vec{\nabla} c - \left(\frac{\partial \mu}{\partial T} \right) \vec{N}_+ \cdot \vec{\nabla} T + \vec{j} \cdot \vec{E} - T \left(\frac{\partial \mu}{\partial T} \right) \vec{\nabla} \cdot \vec{N}_+ \quad (29)$$

The third and last term on the right hand side of Eq. (29) are cancelled by the first one on the right hand side, if we neglect the spatial variation of the thermodynamic derivative $(\partial \mu / \partial T)$. The temperature equation is therefore given by

$$c_p \rho \partial_t T = -\vec{\nabla} \cdot \vec{Q} - \left(\frac{\partial \mu}{\partial c} \right) \vec{N}_+ \cdot \vec{\nabla} c + \vec{j} \cdot \vec{E} \quad (30)$$

Using the constitutive relations (19)–(21), Eq. (30) can be transformed into

$$c_p \rho \partial_t T = \vec{\nabla} \cdot (\lambda \vec{\nabla} T) + \frac{\vec{j}^2}{\kappa} - T \vec{\nabla} \cdot (\beta \vec{j}) + \left(\frac{\partial \mu}{\partial c} \right) \frac{(\vec{N}_+ - (t_+ / Fz_+) \vec{j})^2}{D} - T \vec{\nabla} \cdot \left(c \left(\frac{\partial \mu}{\partial c} \right) \frac{k_T}{T} (\vec{N}_+ - \frac{t_+}{z_+ F} \vec{j}) \right) \quad (31)$$

The temperature changes due to thermal conduction and four different sources for heat. They are in the order of their appearance in Eq. (31): Joule's heat, Thompson effect, heat of mixing and the Soret effect. The Thompson effect can also be written as

$$T \vec{\nabla} \cdot (\beta \vec{j}) = T \frac{\partial \beta}{\partial T} \vec{j} \cdot \vec{\nabla} T := \mu_T \vec{j} \cdot \vec{\nabla} T \quad (32)$$

Here we used charge conservation (Eq (10)) and the Thompson relation for the Thompson coefficient $\mu_T = T (\partial \beta / \partial T)$. If we neglect all contributions proportional to k_T the heat Eq. (31) reduces further to

$$c_p \rho \partial_t T = \vec{\nabla} \cdot (\lambda \vec{\nabla} T) + \frac{\vec{j}^2}{\kappa} - T \vec{\nabla} \cdot (\beta \vec{j}) + \left(\frac{\partial \mu}{\partial c} \right) D (\vec{\nabla} c)^2 \quad (33)$$

The equations for ion concentration, electric field respective electric potential defined by $\vec{E} = -\vec{\nabla} \Phi$ and temperature can be applied in the electrolyte as well as in the active particles. The only difference is the electric conductivity, which is replaced by the average electronic conductivity σ of the solid active particle and carbon black, which is usually used to enhance the electronic conductivity of the electrodes.

2.2. Interface conditions

To couple the transport in electrolyte and active particles we have to formulate interface conditions, which describe the intercalation and deintercalation of ions.

2.2.1. Interface conditions for ionic flux and electric current

The interface conditions describe the intercalation reaction and the deintercalation reaction respectively on the mesoscopic scale (i.e. beyond the scale of the diffuse layer [4]). For one step reactions it is usually assumed that the transport of ions across the interface is completely described by the Butler Volmer approach. More complicated reactions may require the use of more elaborate theories [33], which can be easily incorporated within our theory. Here we use for simplicity the Butler Volmer theory. The current density across the interface i_{se} due to the intercalation reaction is within the Butler Volmer approach given by [4]:

$$i_{se} = i_0 \left(\exp \left[\frac{\alpha_a F}{RT} \eta_s \right] - \exp \left[\frac{-\alpha_c F}{RT} \eta_s \right] \right) \quad (34)$$

α_A and α_C with $\alpha_A + \alpha_C = 1$ are weighting the anodic and the cathodic contribution of the overpotential η_s to the overall reaction. The overpotential is the deviation of the electrochemical potential from the chemical equilibrium between active particle and electrolyte. It is therefore defined by

$$\eta_s := \Phi_s - \Phi_e - \frac{\mu_e - \mu_s}{z_+ F} \quad (35)$$

The overpotential vanishes obviously if the active particle is in equilibrium with the electrolyte. Usually the overpotential is expressed with the help of the half cell open circuit potential U_0 of the respective electrode relative to a Li metal electrode. Without loss of generality setting $\Phi_{Li} = 0$, the open circuit potential U_0 can be written as

$$U_0 = \frac{\mu_{Li} - \mu_s}{z_+ F} \quad (36)$$

Using this expression in Eq. (35) we get

$$\eta_s := \Phi_s - \Phi_e - U_0 - \frac{\mu_e - \mu_{Li}}{z_+ F} \quad (37)$$

Since the chemical potential of the electrolyte μ_e is very different from the chemical potential μ_{Li} of the Li metal electrode the last

two terms in Eq. (37) do not cancel in general. Introducing the electrochemical potential of the electrolyte φ_e relative to the chemical potential of Li - metal

$$\varphi_e := \Phi_e + \frac{\mu_e - \mu_{Li}}{z_+ F} \quad (38)$$

we can rewrite (37) as

$$\eta_s := \Phi_s - \varphi_e - U_0 \quad (39)$$

and obtain the standard form of the overpotential but with the electrochemical potential instead of the electric potential.

The amplitude i_0 in Eq. (34) is given by

$$i_0 = kc^{\alpha_a} c_s^{\alpha_c} (c_{s,max} - c_s)^{\alpha_c} \quad (40)$$

k is a reaction rate. $c_{s,max}$ is the maximum concentration of ions in the active particle. We assume that Li ions are not stored in the double layer (i.e. all Li ions are intercalated in the active particle or released into the electrolyte). There should also be no flux of negative charges across the double layer. Neither enter electrons the electrolyte nor intercalate negative ions from the electrolyte in the active particles under ideal conditions. Both effects would lead to degradation [1], which could of course be modeled by modifying the interface conditions. The absence of flux of negative charges across the interface especially means that the total current across the electrolyte–particle interface is due to transport of positive ions only. If the particle is completely filled i.e. $c = c_{s,max}$, it has to be made sure by the interface conditions that no electrical current \vec{j} is carried by negative charge carriers across the interface. These conditions can be formulated mathematically in the following way with the normal \vec{n} pointing from the solid into the electrolyte:

$$\vec{j}_s \cdot \vec{n} = i_{se} \quad (41)$$

$$\vec{j}_e \cdot \vec{n} = i_{se} \quad (42)$$

$$\vec{N}_{+,s} \cdot \vec{n} = \frac{i_{se}}{z_+ F} \quad (43)$$

$$\vec{N}_{+,e} \cdot \vec{n} = \frac{i_{se}}{z_+ F} \quad (44)$$

2.2.2. Thermal interface conditions

To derive the thermal interface conditions we consider a infinitesimally extended small piece of the interface perpendicular to the normal \vec{n} which points from the active particle into the electrolyte. The interface conditions are most conveniently derived using the form (28) of the heat transport equation. We integrate the temperature balance equation over the infinitesimal small volume element, which contains the whole thickness of double layer. The term proportional to $\vec{\nabla} \cdot \vec{N}_+$ does not contribute to the flux since the flux is conserved across the double layer (see Eq. (43)). We obtain

$$\iiint dV c_p \rho \partial_t T = \iint dA (\vec{n} \cdot (\vec{q}_s - \vec{q}_e) + \vec{n} \cdot \vec{N}_+ (\mu_s - \mu_e) + \vec{n} \cdot \vec{j} (\Phi_s - \Phi_e)) \quad (45)$$

Using Eqs. (41) and (43) and the definition of \vec{Q} we obtain

$$\begin{aligned} \iiint dV c_p \rho \partial_t T = & \iint dA (\vec{n} \cdot (\vec{Q}_s - \vec{Q}_e)) \\ & + \frac{i_{se}}{z_+ F} (\mu_s - \mu_e + z_+ F (\Phi_s - \Phi_e)) \\ & - \frac{i_{se}}{z_+ F} T \left(\frac{\partial \mu_s}{\partial T} - \frac{\partial \mu_e}{\partial T} \right) \end{aligned} \quad (46)$$

If we assume that the double layer instantaneously changes temperature upon changes of the currents, concentrations and temperatures, the double layers is always in a stationary state i.e. the

left hand side of Eq. (46) vanishes. Using Eqs. (36) and (38) we obtain:

$$\vec{n} \cdot (\vec{Q}_s - \vec{Q}_e) = -i_{se} \eta_s - i_{se} T \frac{\partial U_0}{\partial T} - \frac{i_{se}}{z_+ F} T \frac{\partial (\mu_e - \mu_{Li})}{\partial T} \quad (47)$$

Neglecting the temperature dependence of the chemical potential of Li metal and using the constitutive relation for \vec{Q} Eq. (21) we finally obtain:

$$\begin{aligned} & -\lambda_s \vec{n} \cdot \vec{\nabla} T_s + \lambda_e \vec{n} \cdot \vec{\nabla} T_e \\ & = -i_{se} \eta_s - T i_{se} \left\{ (\beta_s - \beta_e) + \frac{\partial (U_0 + \mu_e / (z_+ F))}{\partial T} \right\} \\ & + i_{se} \left(c_s \frac{\partial U_0}{\partial c} k_{T,s} + c_e \frac{\partial \mu_e}{\partial c} k_{T,e} \frac{(1 - t_+)}{z_+ F} \right) \end{aligned} \quad (48)$$

Here we also used that the transference number of Li ions in the active particle may be neglected due to the high mobility of electrons compared to the mobility of Li ions. The physical meaning of the various expressions on the right hand side of Eq. (48) is obvious. The first one is the irreversible heat production due to Joule heating. The next term contributes to the reversible Peltier effect and the last one is the Soret effect in the double layer. The Peltier coefficient is given by

$$\Pi = T(\beta_s - \beta_e) + T \frac{\partial (U_0 + \mu_e / (z_+ F))}{\partial T} \quad (49)$$

Note that in [11] only the partial derivative of the open circuit potential was given as Peltier coefficient. Our rigorous approach shows naturally that also the differences in the Seebeck coefficients of the two phases and the thermal derivative of the electrolytes chemical potential are contributing to the Peltier coefficient. Since our approach is based on experimentally accessible transport coefficients it is either possible to measure directly the Peltier coefficient [34] or to deduce it from measurements of the open circuit potential, the Seebeck coefficients of the two phases [35] and the thermodynamic derivatives of the chemical potential of the electrolyte.

2.3. Closed set of equations for transport in batteries

2.3.1. Electrolyte

The natural variables for the electrolyte are the ion concentration c , the electrical potential Φ_e and the temperature T . Due to the experimentally motivated formulation of the interface conditions with the open circuit potential U_0 relative to a Li metal electrode instead of the difference between chemical potentials of solid particle and electrolyte the electrochemical potential φ (see Eq. (38)) had to be introduced. It is therefore more convenient to formulate the transport equations with φ_e instead of Φ_e . One has to keep in mind that the electric field is still given by $\vec{E} = -\vec{\nabla} \Phi_e = -\vec{\nabla} \varphi_e + \vec{\nabla} \mu_e / (z_+ F)$. The transport equations are then given by

$$\partial_t c_e = \vec{\nabla} \cdot (D_e \vec{\nabla} c_e) - \vec{\nabla} \cdot \left(\frac{t_+}{z_+ F} \vec{j} \right) + \vec{\nabla} \cdot \left(\frac{D c_e k_T}{T} \vec{\nabla} T \right) \quad (50)$$

$$\begin{aligned} 0 = & \vec{\nabla} \cdot (\kappa \vec{\nabla} \varphi_e) - \vec{\nabla} \cdot \left(\kappa \frac{1 - t_+}{z_+ F} \left(\frac{\partial \mu}{\partial c} \right) \vec{\nabla} c_e \right) + \\ & + \vec{\nabla} \cdot \left(\kappa (\beta_e - \frac{1}{z_+ F} \left(\frac{\partial \mu}{\partial T} \right)) \vec{\nabla} T \right) \end{aligned} \quad (51)$$

$$\begin{aligned} c_{p,e} \rho \partial_t T = & \vec{\nabla} \cdot (\lambda_e \vec{\nabla} T) + \frac{\vec{j}^2}{\kappa} - T \vec{\nabla} \cdot (\beta_e \vec{j}) + \\ & + \left(\frac{\partial \mu}{\partial c} \right) \frac{(\vec{N}_+ - \frac{t_+}{z_+ F} \vec{j})^2}{D_e} - T \vec{\nabla} \cdot \left(c_e \left(\frac{\partial \mu}{\partial c} \right) \frac{k_{T,e}}{T} (\vec{N}_+ - \frac{t_+}{z_+ F} \vec{j}) \right) \end{aligned} \quad (52)$$

Note that the first two equations without the terms proportional to the temperature gradients have the form of the equations for the concentrated electrolyte by Newman [4], but it is important to realize that there exists an important quantitative difference. In the concentrated electrolyte theory of [4] the potential in Eq. (51) is interpreted as the electrical potential Φ_e . In our theory the electrical potential had to be replaced by the electrochemical potential φ_e of the electrolyte, if we use the open circuit potential relative to Li metal in the simple expression for the overpotential Eq. (39).

2.3.2. Active particles

Our derivation of the constitutive relations for concentration, electrical potential and temperature is based on general thermodynamic principles and can therefore be applied equally to the transport in active particles. Only if the transport is anisotropical the transport coefficients have to be replaced by tensorial quantities. Here we restrict ourselves to active particles which behave approximately isotropic on the micrometer scale. The equations are slightly simplified due to the reasonable assumption that the transference number can be set to zero, since the electrical current is predominantly electronic of nature. We will denote the electronic conductivity with σ . The transport equations are then given by

$$\partial_t c_s = \vec{\nabla} \cdot (D_s \vec{\nabla} c_s) + \vec{\nabla} \cdot \left(\frac{D c_s k_{T,s}}{T} \vec{\nabla} T \right) \quad (53)$$

$$0 = \vec{\nabla} \cdot (\sigma \vec{\nabla} \Phi_s) + \vec{\nabla} \cdot (\beta_s \sigma \vec{\nabla} T) \quad (54)$$

$$c_{p,s} \rho \partial_t T = \vec{\nabla} \cdot (\lambda_s \vec{\nabla} T) + \frac{j^2}{\sigma} - T \vec{\nabla} \cdot (\beta_s \vec{j}) - z_+ F \frac{\partial U_0}{\partial c} \frac{\vec{N}_+^2}{D_s} + T z_+ F \vec{\nabla} \cdot \left(c_s \frac{\partial U_0}{\partial c} \frac{k_{T,s}}{T} \vec{N}_+ \right) \quad (55)$$

Together with the interface conditions (41)–(44) and (48) the complete set of equations for transport in Li-ion batteries is formulated. Of course the equations have to be closed by using appropriate boundary conditions, but this is standard procedure. They may change from application to application depending on how the cell is coupled to the outside world. Especially different cooling procedure will require different boundary conditions either for the thermal flux or the temperature itself. Also the coupling of the current collector to the electrodes will influence the choice of boundary conditions.

3. Conclusions

We have derived the complete set of transport equations on a spatial scale larger than the diffuse double layer in Li ion batteries. Our derivation is based on general principles of nonequilibrium thermodynamics, which guarantee thermodynamic consistency and especially strictly positive entropy production. The equations for transport in the electrolyte differ from the concentrated electrolyte theory of [4]. It can easily be shown [28], that the concentrated electrolyte theory of [4] violates the Onsager relations. But we have also shown above, that the coupled equations for charge and species transport in Li ion batteries (neglecting heat transport) can be transformed in the form used in [3], [4], if in the electrolyte the pure electrical potential is replaced by the electrochemical potential in combination with the definition (39) for the overpotential.

The complete set of equations can either be used to simulate the transport within cells using a spatial representation of the electrodes, which resolves the microstructure of the porous electrodes or as a starting point to obtain a porous media representation of the electrodes as in [15]. In the microscopic theory active particles

and electrolyte are treated as separate media. So far this approach is only used for simulating the ion and charge transport under isothermal conditions [36,37]. Inclusion of heat transport is planned as future work. The computational complexity of the problem allows only to simulate representative volume elements (REVs) of battery cells. But as post processing effective properties of the porous electrode may be obtained as e.g. effective diffusion coefficients or conductivities by numerically averaging over the REV. These quantities may then be used for simulating the whole cell modeled with the porous electrode model.

So far side reactions as e.g. formation of the solid–electrolyte interface (SEI) or transport within a SEI have not been considered. Within our approach it is straight forward to include those phenomena. Surface reactions will lead to a modification of the interface conditions. Transport within a SEI requires the addition of another thermodynamic phase with appropriate transport coefficients [38]. Volumetric reactions require the inclusion of the reacting species and the information on the reaction kinetics [20]. The derivation of the transport equations will proceed along the same line as shown above with the only difference that the concentrations of the species are not conserved separately but just the sum of them. In future work we will make extensive use of the model to obtain a better understanding of the coupled transport phenomena and their repercussions on the performance and lifetime of Li ion batteries.

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Appendix A. List of symbols

\vec{B}	magnetic induction
D	diffusion constant
$D_{e,s}$	diffusion constant in electrolyte or solid
\vec{D}	electric displacement
\vec{E}	electric field
F	Faraday constant
\vec{H}	magnetic field
M_0, M_{\pm}	molar mass of solvent, Li ion and counterions
\vec{N}_{\pm}	flux of ions or counter ions ($\text{mol m}^{-2} \text{s}^{-1}$)
\vec{Q}	renormalized heat flux (see Eq. (17))
R	entropy production (W m^{-3})
R	universal gas constant ($\text{JK}^{-1} \text{mol}^{-1}$)
T	temperature
U_0	open circuit potential
c	Li ion concentration
c_{\pm}	concentration of Li ions and counter ions (mol m^{-3})
$c_{e,s}$	Li ion concentration in electrolyte or solid
c_p	specific heat per unit mass at constant pressure
e	energy density (J m^{-3})
i_{se}	Butler Volmer flux
i_0	scale of Butler Volmer flux
\vec{j}	electrical current
k	Butler Volmer rate constant
k_B	Boltzmann constant
k_T	Soret–Dufour coefficient
\vec{q}	heat flux (W m^{-2})
s	entropy density (J m^{-3})
z_{\pm}	number of elementary charges per ion or counter ion
$\alpha_{a,c}$	apparent anodic and cathodic transfer coefficients
β	Seebeck coefficient (VK^{-1})

κ	ionic conductivity
λ	heat conductivity ($\text{W K}^{-1} \text{m}^{-1}$)
μ	collective chemical potential of Li ions (see Eq. (6))
μ_0, μ_{\pm}	chemical potential of neutral, positive and negative phase
μ_T	Thompson coefficient (V K^{-1})
φ	electrochemical potential of electrolyte
ρ	mass density (kg m^{-3})
ρ_{el}	charge density (C m^{-3})
σ	electronic conductivity
Φ	electrical potential
Π	Peltier coefficient (V)

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