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On the role of saturation in modeling ionic transport in the electrolyte of (Lithium ion) batteries

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HIGHLIGHTS

- We developed a novel approach in modeling ionic transport in the electrolyte.
- We considered fundamental laws with no recourse to electroneutrality equation.
- Constitutive theory, weak forms, simulations are framed in a rigorous PDEs setting.
- Saturation in the electrolyte is considered and its impact analyzed.
- Results show that saturation might significantly impact on the electric potential.

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ABSTRACT

Recent computational simulations of ionic conductivity across the electrolyte of commercial batteries by Salvadori et al. (2015) have shown that the concentration of ions exceeds half the saturation limit near the electrodes. This observation, which is in agreement with other approaches by Danilov and Notten (2008), implies that the widespread assumption of infinite dilution far from saturation is questionable. The present contribution is therefore devoted to investigate the role of saturation in modeling ionic transport in the electrolyte of Li-ion batteries. An important result is found, that saturation has no effect on the diffusivity, whereby the condition of electroneutrality is well approximated in the solution. However saturation affects the electric potential up to 40% near the electrodes for all charge rates.

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1. Introduction

Consider an electrochemical cell with a binary ionic electrolyte (say LiX, where X can for instance [3] be PF₆, consisting of two ions, a cation (Li⁺) and an anion (X[−])). In the absence of convection, ions are transported by migration and diffusion across the electrolyte from one electrode to the other, to bring reactants to the interfaces so that electrochemical charge transfer reactions can take place. Modeling the kinetics of mobile ionic species in the electrolyte is

thus required in order to perform predictive computational simulations of electrochemical cells.

A vast amount of literature is available on the mathematical modeling of charge transport in batteries: one can refer to the reviews [4,5] for an extensive bibliographic analysis. Ionic species kinetics was recently considered in Ref. [1]. That paper presents a formulation based on: i) the mass continuity equation for the cations Li⁺ and anions X[−], in terms of their concentrations c_{Li^+} and c_{X^-} ; ii) Maxwell's equations, to model the evolution in time and space of the electric field, since ionic transport entails movement of mass as well as of charge. Electroneutrality was not used as a fundamental law – as in Refs. [6,7] – and electro-magnetics was explicitly taken into account via the *electro-quasi-static* formulation [8] of Maxwell's equations. A one-dimensional application to ionic transport

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in Li-ion batteries electrolyte, inspired by Refs. [2], was performed.

While the outcome matches the results published in Refs. [2], it turned out that ionic concentrations near the electrodes can be higher than half of the *saturation limit* in the electrolyte solution. Therefore the usual and widespread simplified form of the chemical Helmholtz free energy density due to mixing of the species¹ does not seem to be suitable for commercial Li-ion batteries. The significant role played by the saturation contribution in the Helmholtz free energy density is therefore investigated in detail in the present paper.

Mass balance as well as Faraday's and Maxwell's equations are recalled briefly in Section 3. Balance laws are considered to be not affected by the saturation,² i.e. there is no supply of species and the degree of dissociation of the binary salt in the solution is complete. The latter condition may not be satisfied in reality *when concentrations are close to the saturation limit*. In those cases it is known from literature that the degree of dissociation of Li-salts dissolved in an organic solvent is incomplete. Modeling the dissociation rate would require a bulk term in the mass balance equations and an additional mass balance equation for the undissociated salt [2]. The numerical analyses in Ref. [1] reveal that concentration peaks exceed 50% of the saturation limit. Concentrations are therefore too high to neglect the role of saturation but they are nevertheless sufficiently far from saturation to assume complete dissociation of the Li-salt.

A rigorous analysis of general principles of thermodynamics is performed in Section 4 following the approach described in Refs. [9,10] for processes in thermal equilibrium. The entropy imbalance and the Coleman-Noll procedure provide thermodynamic restrictions which are satisfied by the usual Fickian description of diffusion and migration in terms of the electrochemical potential, as defined in Refs. [11,12]. Dilute solutions have been implemented taking into account the saturation limit. The formulation does not consider mixing with interactions (regular solutions) nor concentrated solutions (modeled by the Maxwell–Stefan equations of multicomponent diffusion – see appendix B). Extension to those conditions, although out of the scope of the present contribution, appears to be straightforward.

A weak form of the governing equations has been derived in Section 6 in terms of the selected thermodynamic fields, namely concentrations and the electric potential. A one-dimensional application to ionic transport in Li-ion batteries, inspired by Refs. [2], is performed thereafter. Results with and without saturation are compared, and the role of saturation is clearly identified.

2. The electroneutrality approximation

Any electric charge in the electrolyte is due to an unbalance of concentration between positive Li^+ and negative X^- ions that are transported across the electrolyte. Apart from narrow layers³ termed after Helmholtz, Stern and the Gouy-Chapman, the deviation from electroneutrality is very small. Numerical analyses quantify the deviation to be about ten orders of magnitude smaller than the equilibrium electrolyte concentration (see Refs. [13], page 286, for instance, and Fig. 2-e in Section 7).

The *electroneutrality condition*

$$c_{\text{Li}^+} - c_{\text{X}^-} = 0 \quad (1)$$

¹ That was used implicitly in Ref. [2] and explicitly in Ref. [1].

² It mainly affects the constitutive equations.

³ According to the literature [13], the size of such a diffuse double layer structure is in the order of 10 to 20 nm.

Fig. 1. A one-dimensional model of a Li-ion battery, with separator of size $l = 2.8 \times 10^{-4} \text{m}$. The flux of Li^+ ions during charge is indicated.

incorporates this numerical evidence and is widely used. It dictates that neutrality is maintained in the solution⁴ since charges cannot be separated. Equation (1) allowed the development of well known theories as Newman's one, but once used in place of Maxwell's equations it does not allow to recover the energy description of the electromagnetic interactions. For this reason it is not compatible with multi-scale approaches. Accordingly, following [15] a different modeling approach has been pursued, whereby equation (1) is no longer used as a fundamental law. In the present note, the electro-magnetics is explicitly taken into account via the *electro-quasi-static* formulation [8] of Maxwell's equations, which is summarized in Section 3.

3. Balance laws

3.1. Mass balance

The mass balance equation may be written as follows

$$\frac{\partial c_\alpha}{\partial t} + \text{div} \left[\vec{h}_\alpha \right] = 0 \quad (2)$$

In this equation, c_α is the *molarity* (i.e. the number of moles per unit volume) of a generic species α ; $\vec{h}_\alpha$ is the mass flux in terms of moles, i.e. the number of moles of species α measured per unit area per unit time. In the problem at hand, eq. (2) applies to ions Li^+ and X^- , i.e.

$$\frac{\partial c_{\text{Li}^+}}{\partial t} + \text{div} \left[\vec{h}_{\text{Li}^+} \right] = 0 \quad (3a)$$

$$\frac{\partial c_{\text{X}^-}}{\partial t} + \text{div} \left[\vec{h}_{\text{X}^-} \right] = 0 \quad (3b)$$

Concentrations are defined in space $\vec{x} \in V$ and time $0 \leq t \leq t_f$, i.e. $c_\alpha = c_\alpha(\vec{x}, t)$. Functional dependence however is specified when necessary only, to enhance readability.

3.2. Faraday's law

Charges in the electrolyte solution are transported by dissociated ions. Therefore, the charge density ζ is related to the concentration of ions, by the following identity:

$$\zeta = F \sum_\alpha z_\alpha c_\alpha \quad (4a)$$

$F = 96485.3383 \text{ C mol}^{-1}$ is Faraday's constant and z_α is the number of electrons transferred per ion α , typically +1 for Li^+

⁴ An excellent discussion on the origin of equation (1) can be found in Ref. [14] in terms of the Debye length.

Fig. 2. Concentration plots. a-c) Lithium ions concentration profiles $c_{\text{Li}^+}(x, t)$ at different C-rates. In all cases the concentration at the initial time equals c_{bulk} , thus satisfying thermodynamic equilibrium. For high C-rates, the steady state configuration cannot be attained, since the limit condition of vanishing concentration at an electrode is reached earlier. d) Concentration profiles with saturation for a galvanostatic process at different C-rates at Cathode (upper, shadowed area) and Anode. For C-rates greater or equal to 2 the limit condition of vanishing concentration at an electrode is reached and the steady state conditions cannot be attained. e) Scattering of the absolute value of the difference in concentration along the electrolyte between positive and negative ions as a measure of electroneutrality. Different colors indicate different times. f) Scattering of the absolute value of the difference in concentration along the electrolyte between the solutions with and without saturation for a galvanostatic process at unit C-rate. Different colors indicate different times.

cations and -1 for X^- anions. The flux of mass in balance (2) of each species contributes to a current density $\vec{i}$ in view of Faraday's law of electrolysis

$$\vec{i} = F \sum_{\alpha} z_{\alpha} \vec{h}_{\alpha} = F (\vec{h}_{\text{Li}^+} - \vec{h}_{\text{X}^-}) \quad (4b)$$

3.3. Maxwell's equations for electro-quasi-statics

Gauss's laws

$$\text{div} [\vec{D}] = \zeta \quad (5)$$

$$\text{div} [\vec{B}] = 0 \quad (6)$$

relate the electric displacement and magnetic fields ($\vec{D}$ and $\vec{B}$ respectively) emanating from a distribution of electric charge ζ . Maxwell-Faraday's law of induction describes the reciprocal interactions between magnetic and electric field $\vec{E}$, in the form

$$\text{curl} [\vec{E}] = -\frac{\partial \vec{B}}{\partial t} \quad (7)$$

In view of (7), the electric field can be written in terms of a so-called "magnetic potential" $\vec{A}$ and of an electrostatic potential ϕ as

$$\vec{E} = -\nabla[\phi] - \frac{\partial \vec{A}}{\partial t}$$

In the framework of electro-quasi-statics [8], assumed henceforth as an approximation of the full Maxwell's equations, the magnetic potential $\vec{A}$ is time-independent. Accordingly, the electric field is irrotational:

$$\vec{E} = -\nabla[\phi] \quad (8)$$

Finally, Ampère's law (with Maxwell's correction)

$$\frac{\partial \vec{D}}{\partial t} + \vec{i} = \text{curl} [\vec{H}] \quad (9)$$

relates the electrical current and the time variation of the electric displacement field to the magnetizing field $\vec{H}$. After application of

the divergence operator and of Faraday's law (4b), the following equation results:

$$\operatorname{div} \left[\frac{\partial \vec{D}}{\partial t} + F(\vec{h}_{\text{Li}^+} - \vec{h}_{\text{X}^-}) \right] = 0 \quad (10)$$

Note that the effect of the latter in Ampère's law cannot be disregarded even in the simplified framework of electro-quasistatics, see Ref. [16].

4. Thermodynamics

The first law of thermodynamics represents the balance of the interplay between the internal energy of a material region $\mathcal{P}$, the power expended on $\mathcal{P}$, the heat transferred in $\mathcal{P}$, and the power due to mass and electromagnetic interactions exchanged on $\mathcal{P}$. Without taking into account the mechanical external power expended on $\mathcal{P}$, the energy balance reads:

$$\frac{\partial \mathcal{U}}{\partial t}(\mathcal{P}) = \mathcal{Q}(\mathcal{P}) + \mathcal{T}(\mathcal{P}) + \mathcal{E}(\mathcal{P}) \quad (11)$$

denoting the net internal energy of $\mathcal{P}$ with $\mathcal{U}$, the power due to heat transfer with $\mathcal{Q}$, the power due to mass transfer with $\mathcal{T}$, the power due to electromagnetic interactions with $\mathcal{E}$. It is assumed that the *energies due to charges and mass transfer are additively treated* as two separate processes, and more broadly that all processes are accompanied with their own *separate energy contribution* in the balance. The individual contributions read:

$$\mathcal{Q}(\mathcal{P}) = \int_{\mathcal{P}} s_q d\Omega - \int_{\partial\mathcal{P}} \vec{q} \cdot \vec{n} d\Gamma \quad (12a)$$

$$\mathcal{T}(\mathcal{P}) = \sum_{\alpha} \left\{ \int_{\mathcal{P}} \mu_{\alpha} s_{\alpha} d\Omega - \int_{\partial\mathcal{P}} \mu_{\alpha} \vec{h}_{\alpha} \cdot \vec{n} d\Gamma \right\} \quad (12b)$$

$$\mathcal{E}(\mathcal{P}) = - \int_{\partial\mathcal{P}} (\vec{E} \times \vec{H}) \cdot \vec{n} d\Gamma \quad (12c)$$

The time variation of the net internal energy corresponds to the power expended by external agencies: a heat contribution where the scalar s_q is the heat supplied by external agencies and $\vec{q}$ is the heat flux vector; a mass flux contribution with the scalar μ denoting the *chemical potential*, the scalar s_{α} the supply of species ($\alpha = \text{Li}^+, \text{X}^-$) and $\vec{h}_{\alpha}$ the mass flux vector; an electromagnetic contribution with the energy flux vector $\vec{E} \times \vec{H}$ generated by the electric and magnetizing fields.⁵

As usual in thermodynamics of continua one can write the local form of the first principle in terms of rates of the specific internal energy u per unit volume

$$\mathcal{U}(\mathcal{P}) = \int_{\mathcal{P}} u d\Omega$$

Standard application of the divergence theorem, of mass balances (2), and of the following definition of chemical potential

$$\bar{\mu}_{\alpha} = \mu_{\alpha} + Fz_{\alpha}\phi \quad (13)$$

leads from (12) to the local form of the first principle in terms of rates of the internal energy u :

$$\frac{\partial u}{\partial t} = s_q - \operatorname{div} [\vec{q}] - \operatorname{div} \left[\phi \frac{\partial \vec{D}}{\partial t} \right] + \sum_{\alpha} \bar{\mu}_{\alpha} \frac{\partial c_{\alpha}}{\partial t} - \vec{h}_{\alpha} \cdot \nabla [\bar{\mu}_{\alpha}] \quad (14)$$

A detailed description can be found in [appendix A](#).

A local form of the entropy imbalance can be derived from the Clausius-Duhem inequality in terms of the entropy η and of the absolute temperature T [9]:

$$\frac{\partial \eta}{\partial t} - \frac{s_q}{T} + \operatorname{div} \left[\frac{\vec{q}}{T} \right] \geq 0 \quad (15)$$

The entropy imbalance can be expressed in terms of internal energy in the form (14) – see [Appendix A](#). By applying the Coleman-Noll procedure, the following thermodynamic restrictions finally arise:

$$T - \frac{\partial u}{\partial \eta} = 0, \quad \mu_{\alpha} - \frac{\partial u}{\partial c_{\alpha}} = 0, \quad \vec{E} - \frac{\partial u}{\partial \vec{D}} = 0,$$

$$\vec{h}_{\alpha} \cdot \nabla [\bar{\mu}_{\alpha}] \leq 0, \quad \frac{1}{T} \vec{q} \cdot \nabla [T] \leq 0 \quad (16)$$

Different thermodynamic potentials can be considered rather than the internal energy u . The specific *Helmholtz free energy*

$$\psi(T, c_{\alpha}, \vec{E}) = u(\eta, c_{\alpha}, \vec{D}) - T\eta - \vec{E} \cdot \vec{D}$$

will be used henceforth.

5. Constitutive theory

The processes are taken to be thermodynamically uncoupled and the Helmholtz free energy density ψ is decomposed in two separate parts:

$$\psi(\epsilon, c_{\alpha}, \vec{E}) = \psi_{\text{diff}}(c_{\alpha}) + \psi_{\text{el}}(\vec{E}) \quad (17)$$

The mass transport process is described by ψ_{diff} , adopting species concentrations c_{α} , as the state variables. The contribution $\psi_{\text{el}}(\vec{E})$ models the electro-quasistatic interactions, in terms of the electric field $\vec{E}$.

The electric displacement field is taken to be linearly related to the electric field

$$\psi_{\text{el}}(\vec{E}) = -\frac{1}{2} \epsilon \vec{E} \cdot \vec{E} \quad (18)$$

where

$$\vec{D} = \epsilon \vec{E} = -\epsilon \nabla [\phi] \quad (19)$$

The permittivity ϵ of a homogeneous material is usually given relative to that of vacuum $\epsilon_0 = 8.85 \times 10^{-12} \text{ CV}^{-1} \text{ m}^{-1}$, as a relative permittivity ϵ_r , i.e. $\epsilon = \epsilon_r \epsilon_0$.

The electrostatic potential ϕ is the result of idealized electric charges moving from one electrode to the other, modeled by Fickian-diffusion that linearly correlates the mass flux of species α to the gradient of its *electrochemical potential*:

$$\vec{h}_{\alpha} = -\mathbf{M}_{\alpha} \nabla [\bar{\mu}_{\alpha}] \quad (20)$$

by means of a positive definite mobility tensor $\mathbf{M}_{\alpha}$. Identity (20) satisfies thermodynamic restrictions (16). A classical specialization of mobility tensor $\mathbf{M}_{\alpha}$ for *dilute solutions accounting for saturation* is

⁵ It actually results from Poynting's theorem (see also [10,11]).

the isotropic non linear case [17].

$$M_{\alpha}(c_{Li^{+}}, c_{X^{-}}) = \psi_{\alpha} c_{\alpha} (1 - \theta_{Li^{+}} - \theta_{X^{-}}) \mathbb{1} \quad \alpha = Li^{+}, X^{-} \quad (21)$$

The amount $\psi_{\alpha} > 0$ is usually termed the *ion mobility* and represents the average velocity of species α in the solution when acted upon by a force of 1 N/mol independent of the origin of the force⁶; θ_{α} is defined as the ratio $\theta_{\alpha} = \frac{c_{\alpha}}{c_{max}}$, where c_{max} stands for the cumulative saturation limit for ions Li^{+} and X^{-} in the solution, in condition of electroneutrality. Equation (21) represents the physical requirement that both the pure ($c_{\alpha}=0$) and the saturated ($\theta_{Li^{+}} + \theta_{X^{-}} = 1$) phases have vanishing mobilities in the electrolyte. It can be seen as a special case of the Maxwell–Stefan approach (see Appendix B). Exploiting the electroneutrality condition (1), the specialization for the mobility tensor simplifies to

$$M_{\alpha}(c_{\alpha}) = \psi_{\alpha} c_{\alpha} \left(1 - 2 \frac{c_{\alpha}}{c_{max}}\right) \mathbb{1} \quad (22)$$

The free energy $\psi_{diff}(c_{\alpha})$ in a mixture depends on the composition of the mixture itself.⁷ Guided by the numerical analyses in Refs. [1,2], where it was shown that concentration peaks amount to about 50% of the saturation limit, the modeling assumption is here taken that *concentrations are sufficiently far from saturation to disregard energetic interactions in the solution yet not small enough to neglect the saturation contribution*. The free energy thus reads:

$$\begin{aligned} \psi_{diff}(c_{Li^{+}}, c_{X^{-}}) = & \mu_{Li^{+}}^0 c_{Li^{+}} + \mu_{X^{-}}^0 c_{X^{-}} + RTc^{max}(\theta_{Li^{+}} \ln[\theta_{Li^{+}}] \\ & + \theta_{X^{-}} \ln[\theta_{X^{-}}]) + RTc^{max}(1 - \theta_{Li^{+}} - \theta_{X^{-}}) \ln[(1 \\ & - \theta_{Li^{+}} - \theta_{X^{-}})] \end{aligned} \quad (23)$$

In formula above, R is the universal gas constant; μ_{α}^0 is a reference value of the chemical potential of diffusing species $\alpha=Li^{+}, X^{-}$. By exploiting electroneutrality (1), the chemical potential results in the form

$$\mu_{\alpha} = \mu_{\alpha}^0 + RT \ln \left[\frac{c_{\alpha}}{c_{max} - 2c_{\alpha}} \right] \quad (24)$$

thus leading to the following expression for the mass flux:

$$\vec{h}_{\alpha} = -D_{\alpha} \nabla [c_{\alpha}] - z_{\alpha} F \psi_{\alpha} c_{\alpha} \left(1 - 2 \frac{c_{\alpha}}{c_{max}}\right) \nabla [\phi] \quad (25)$$

D_{α} is defined by $D_{\alpha} = \psi_{\alpha} RT$ (this equation is sometimes termed after Nernst–Einstein). By comparing (25) with the mass flux formula for infinitely diluted solutions

$$\vec{h}_{\alpha} = -D_{\alpha} \nabla [c_{\alpha}] - z_{\alpha} F \psi_{\alpha} c_{\alpha} \nabla [\phi] \quad (26)$$

one concludes that saturation has no effect on the diffusivity: in fact, the impact of saturation on the mobility tensor (22) and on the chemical potential (24) counteract each other in the evaluation of diffusivity.⁸ Saturation does affect the electric contribution in the mass flux (25) by changing the mobility, thus creating either a lower mass flux at a given potential gradient or a higher potential gradient at a given flux.

6. Governing equations and weak form

Governing equations can be derived by incorporating constitutive equations (19) and (25) into balance equations. The unknown fields result from the thermodynamic choices made. They are here the concentrations $c_{Li^{+}}$, $c_{X^{-}}$, and the electric potential ϕ . Governing equations hold at all points $\vec{x} \in V$ in all instants of interval $[0, t]$:

$$\frac{\partial c_{Li^{+}}}{\partial t} + \text{div} \left[-D_{Li^{+}} \nabla [c_{Li^{+}}] - F \psi_{Li^{+}} c_{Li^{+}} \left(1 - 2 \frac{c_{Li^{+}}}{c_{max}}\right) \nabla [\phi] \right] = 0 \quad (27a)$$

$$\frac{\partial c_{X^{-}}}{\partial t} + \text{div} \left[-D_{X^{-}} \nabla [c_{X^{-}}] + F \psi_{X^{-}} c_{X^{-}} \left(1 - 2 \frac{c_{X^{-}}}{c_{max}}\right) \nabla [\phi] \right] = 0 \quad (27b)$$

$$\begin{aligned} \text{div} \left[-\frac{1}{\epsilon} \nabla \left[\frac{\partial \phi}{\partial t} \right] + F (D_{X^{-}} \nabla [c_{X^{-}}] - D_{Li^{+}} \nabla [c_{Li^{+}}]) \right] + \\ - F^2 \text{div} \left[\left(\psi_{Li^{+}} c_{Li^{+}} \left(1 - 2 \frac{c_{Li^{+}}}{c_{max}}\right) + \psi_{X^{-}} c_{X^{-}} \left(1 - 2 \frac{c_{X^{-}}}{c_{max}}\right) \right) \nabla [\phi] \right] = 0 \end{aligned} \quad (27c)$$

under the constraints

$$c_{Li^{+}} > 0 \quad (28a)$$

$$c_{X^{-}} > 0 \quad (28b)$$

The difference between equations (25) and (26) makes this set of governing equations different from the one used in Ref. [1]. Boundary conditions

$$\vec{h}_{Li^{+}} \cdot \vec{n} = -h_{BV} \quad \vec{x} \in \partial^N V \quad (29a)$$

$$\vec{h}_{X^{-}} \cdot \vec{n} = 0 \quad \vec{x} \in \partial^N V \quad (29b)$$

$$\text{curl} [\vec{H}] \cdot \vec{n} = -F h_{BV} \quad \vec{x} \in \partial^N V \quad (29c)$$

are imposed along Neumann boundaries⁹ $\partial^N V$. It is typical in batteries to fully impose Neumann conditions (29a) for concentration, in terms of mass fluxes, during galvanostatic processes. To complete the problem, Dirichlet boundary conditions have to be enforced along part $\partial^D V$, ($\partial V = \partial^D V \cup \partial^N V$). Zero electric potential have to be included through Dirichlet boundary conditions. Initial conditions are required for the concentration of ions $c_{Li^{+}}(\vec{x}, t=0)$ and $c_{X^{-}}(\vec{x}, t=0)$ in the electrolyte solution. As at time $t=0$ thermodynamic equilibrium holds, concentrations are uniform and obey the electroneutrality condition (1) in volume V . Consistently, a positive constant c_{bulk} will be defined as

$$c_{bulk} = c_{Li^{+}}(\vec{x}, t=0) = c_{X^{-}}(\vec{x}, t=0) \quad (30)$$

This constant will further be used to scale concentrations.

Initial conditions for electric potential and displacements define a boundary value problem at $t=0$. In view of the perfect electroneutrality, Gauss law provides the necessary and sufficient equation to be solved for ϕ at $t=0$:

⁶ As the free energy density ψ has been selected as the thermodynamic potential, no source of confusion between the ion mobility ψ_{α} and the internal energy density u will arise henceforth.

⁷ The case of diluted (in the sense of [11]) solutions will be considered henceforth whereas other theories will be summarized in Appendices.

⁸ The role played by the non linear mobility tensor and by the free energy density at saturation in Fick's law (25) is further investigated in appendix C.

⁹ Boundary conditions (29a) and (29c) have been derived in Section 3.3 of [1]. Extension of Neumann boundaries are defined for each field and differ from field to field. In order to enlighten the notation the field dependence has not been specified in writing $\partial^N V$ and has been omitted. Same arguments apply to Dirichlet boundaries.

$$\operatorname{div} [\mathfrak{d} \nabla [\phi]] = 0 \quad \vec{x} \in V, t = 0 \quad (31a)$$

together with the usual homogeneous boundary conditions for potential and current, in view of thermodynamic equilibrium at initial time. The evolution problem can be formulated in a weak form by multiplying the governing equation (27) by a suitable set of test functions and performing an integration over the domain, exploiting Green's formula to reduce the order of differentiation. Adopting a Galerkin approach, weak forms are built using variations (denoted henceforth with symbol $\hat{\cdot}$) of the same variables that rule the problem, namely concentrations $\hat{c}_{Li^+}$, $\hat{c}_{X^-}$, and electric potential $\hat{\phi}$. The following identities are derived straightforwardly:

$$\begin{aligned} \frac{RT}{c_{bulk}} \int_V \hat{c}_{Li^+} \left\{ \frac{\partial c_{Li^+}}{\partial t} + \operatorname{div} [\vec{h}_{Li^+}] \right\} dV = \\ \frac{RT}{c_{bulk}} \int_V \hat{c}_{Li^+} \frac{\partial c_{Li^+}}{\partial t} + \mathbb{D}_{Li^+} \nabla [\hat{c}_{Li^+}] \cdot \nabla [c_{Li^+}] + F \Psi_{Li^+} c_{Li^+} \left(1 - 2 \frac{c_{Li^+}}{c_{max}} \right) \nabla [\hat{c}_{Li^+}] \cdot \nabla [\phi] dV + \\ - \frac{RT}{c_{bulk}} \int_{\partial^N V} \hat{c}_{Li^+} h_{BV} d\Gamma = 0 \end{aligned} \quad (32a)$$

$$\begin{aligned} \frac{RT}{c_{bulk}} \int_V \hat{c}_{X^-} \left\{ \frac{\partial c_{X^-}}{\partial t} + \operatorname{div} [\vec{h}_{X^-}] \right\} dV = \\ \frac{RT}{c_{bulk}} \int_V \hat{c}_{X^-} \frac{\partial c_{X^-}}{\partial t} + \mathbb{D}_{X^-} \nabla [\hat{c}_{X^-}] \cdot \nabla [c_{X^-}] - F \Psi_{X^-} c_{X^-} \left(1 - 2 \frac{c_{X^-}}{c_{max}} \right) \nabla [\hat{c}_{X^-}] \cdot \nabla [\phi] dV = 0 \end{aligned} \quad (32b)$$

$$\begin{aligned} \int_V \hat{\phi} \operatorname{div} \left[\frac{\partial \vec{D}}{\partial t} + F (\vec{h}_{Li^+} - \vec{h}_{X^-}) \right] dV = \\ \int_V \nabla [\hat{\phi}] \cdot \left\{ \mathfrak{d} \nabla \left[\frac{\partial \phi}{\partial t} \right] + F^2 \left(\Psi_{Li^+} c_{Li^+} \left(1 - 2 \frac{c_{Li^+}}{c_{max}} \right) + \Psi_{X^-} c_{X^-} \left(1 - 2 \frac{c_{X^-}}{c_{max}} \right) \right) \nabla [\phi] \right\} dV + \\ - F \int_V \nabla [\hat{\phi}] \cdot (\mathbb{D}_{X^-} \nabla [c_{X^-}] - \mathbb{D}_{Li^+} \nabla [c_{Li^+}]) dV - F \int_{\partial^N V} \hat{\phi} h_{BV} d\Gamma = 0 \end{aligned} \quad (32c)$$

Boundary conditions (29a) and (29c) have been used. The mass balance equation (32a) has been scaled by coefficient $\frac{RT}{c_{bulk}}$, deriving from constitutive equation (24), to give to the new weak form the physical dimension of a power expenditure.

Fields that govern the problem are scaled to make them dimensionless and of order one:

$$c_{\alpha}^* = \frac{c_{\alpha}}{c_{bulk}}, \quad \phi^* = \frac{F}{RT} \phi, \quad (33)$$

L stands for a given characteristic length. A dimensionless weak form can finally be given in a time interval $[0, t_f]$ as.

Find $y^*(\vec{x}, t) \in \mathcal{Y}^{[0, t_f]}$ such that

$$\begin{aligned} \frac{d}{dt} b^*(\hat{y}^*(\vec{x}), y^*(\vec{x}, t)) + a^*(\hat{y}^*(\vec{x}), y^*(\vec{x}, t)) \\ = f^*(\hat{y}^*(\vec{x})) \forall \hat{y}^*(\vec{x}) \in \mathcal{Y} \end{aligned} \quad (34)$$

where

$$\begin{aligned} b^*(\hat{y}^*(\vec{x}), y^*(\vec{x}, t)) &= RT c_{bulk} \int_V \hat{c}_{Li^+}^* c_{Li^+}^* + \hat{c}_{X^-}^* c_{X^-}^* dV + \mathfrak{d} \left(\frac{RT}{F} \right)^2 \int_V \nabla [\hat{\phi}^*] \cdot \nabla [\phi^*] dV \\ a^*(\hat{y}^*(\vec{x}), y^*(\vec{x}, t)) &= \\ &RT c_{bulk} \mathbb{D}_{Li^+} \int_V \nabla [\hat{c}_{Li^+}^*] \cdot \nabla [c_{Li^+}^*] + c_{Li^+}^* \left(1 - 2 \frac{c_{Li^+}^*}{c_{max}^*} \right) \nabla [\hat{c}_{Li^+}^*] \cdot \nabla [\phi^*] dV + \\ &RT c_{bulk} \mathbb{D}_{X^-} \int_V \nabla [\hat{c}_{X^-}^*] \cdot \nabla [c_{X^-}^*] - c_{X^-}^* \left(1 - 2 \frac{c_{X^-}^*}{c_{max}^*} \right) \nabla [\hat{c}_{X^-}^*] \cdot \nabla [\phi^*] dV + \\ &RT c_{bulk} \mathbb{D}_{Li^+} \int_V \nabla [\hat{\phi}^*] \cdot \nabla [\phi^*] \left(1 - 2 \frac{c_{Li^+}^*}{c_{max}^*} \right) c_{Li^+}^* + \nabla [\hat{\phi}^*] \cdot \nabla [c_{Li^+}^*] dV + \\ &RT c_{bulk} \mathbb{D}_{X^-} \int_V \nabla [\hat{\phi}^*] \cdot \nabla [\phi^*] \left(1 - 2 \frac{c_{X^-}^*}{c_{max}^*} \right) c_{X^-}^* - \nabla [\hat{\phi}^*] \cdot \nabla [c_{X^-}^*] dV \\ f^*(\hat{y}^*(\vec{x})) &= RT \int_{\partial^N V} (\hat{\phi}^* + \hat{c}_{Li^+}^*) h_{BV} d\Gamma \end{aligned}$$

Fig. 3. Potential profile with and without saturation for a galvanostatic process at different C-rates at Cathode. The electric potential at the Anode is arbitrarily set to zero.

with $y^*(\vec{x}, t) = \{c_{Li^+}^*, c_{X^-}^*, \phi^*\}$. Constraints (28) still apply.

7. One-dimensional modeling of ionic transport in a fluid electrolyte

7.1. Description

A battery with a storage capacity of 720mAh is dealt with, see Ref. [1]. It undergoes a galvanostatic process of charge at different C-rates (0.25, 0.5, 1, 2, and 4). The electrolyte is supposed to have a saturation limit for $LiPF_6$ of 5000 mol m^{-3} (hence $c^{max} = 10^4 \text{ mol m}^{-3}$). How saturation affects the battery performances is analyzed next. As in Ref. [2], mechanical effects are not taken into account. The charge/discharge process is assumed to be isothermal at $T = 25^\circ\text{C}$.

The current $I(t)$ (with t in seconds) is tuned in time as

$$I(t) = (1 - e^{-t}) I_{nC} \quad (35)$$

I_{nC} stands for the steady current at a C-rate equal to n . The concentration of ions across the electrolyte is uniform at $t = 0$ and amounts to $c_{bulk} = 1500 \text{ mol m}^{-3}$. The flux of Lithium ions at the electrodes/separator interfaces (with net area $A = 2 \times 10^{-2} \text{ m}^2$) is related to the given current $I(t)$ flowing through the battery. A uniform ionic flow at the interfaces is considered, enabling a 1D description. Boundary conditions (29) thus read:

reads

$$h_{1C} = -\frac{I_{nC}}{FA}$$

Diffusivities are given by $D_{Li^+} = 2 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$, $D_{PF_6^-} = 3 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$. The separator thickness is $l = 280 \text{ } \mu\text{m}$. All data are taken from Ref. [2] except from the relative permittivity, taken equal to $\epsilon_r = 95$ from Ref. [18].

7.2. Discretization and time advancing by finite differences

Discretization is performed by separating variables, with spatial test $\varphi_i(x)$ and shape functions $\varphi_j(x)$ and nodal unknowns (collectively gathered in column y with component $y_j(t)$) that depend solely on time. The weak form (34) is then transformed in a first order Ordinary Differential Equation (ODE) in time¹⁰, which reads:

$$\text{Find } y(t) \text{ s.t. } b_i^* \cdot \dot{y}(t) + a_i^* \cdot y(t) + {}^{sat} a_i^* [y(t)] = f_i^*(t) \quad (37)$$

for $i = 1, 2, \dots, N$

Operators b_i^* and a_i^* are not influenced by the saturation of the electrolyte and coincide with those used in Ref. [1], given by

$$\begin{aligned} \frac{1}{RT c_{bulk}} b_i^* \cdot \frac{\partial y}{\partial t}(t) &= \int_0^l \varphi_i^{Li^+} \varphi_j^{Li^+} dx \frac{\partial c_j^{Li^+}}{\partial t} + \int_0^l \varphi_i^{X^-} \varphi_j^{X^-} dx \frac{\partial c_j^{X^-}}{\partial t} + \frac{\epsilon}{c_{bulk}} \frac{RT}{F^2} \int_0^l \frac{\partial \varphi_i^\phi}{\partial x} \frac{\partial \varphi_j^\phi}{\partial x} dx \frac{\partial \phi_j}{\partial t} \\ \frac{a_i^*[y(t)]}{RT c_{bulk}} &= D_{Li^+} \int_0^l \frac{\partial \varphi_i^{Li^+}}{\partial x} \frac{\partial \varphi_j^{Li^+}}{\partial x} dx c_j^{Li^+} + D_{Li^+} \int_0^l \varphi_j^{Li^+} \frac{\partial \varphi_i^{Li^+}}{\partial x} \frac{\partial \varphi_k^\phi}{\partial x} dx c_j^{Li^+} \phi_k + \\ &D_{X^-} \int_0^l \frac{\partial \varphi_i^{X^-}}{\partial x} \frac{\partial \varphi_j^{X^-}}{\partial x} dx c_j^{X^-} - D_{X^-} \int_0^l \varphi_j^{X^-} \frac{\partial \varphi_i^{X^-}}{\partial x} \frac{\partial \varphi_k^\phi}{\partial x} dx c_j^{X^-} \phi_k + \\ &D_{Li^+} \int_0^l \frac{\partial \varphi_i^\phi}{\partial x} \frac{\partial \varphi_k^\phi}{\partial x} \varphi_j^{Li^+} dx c_j^{Li^+} \phi_k + D_{Li^+} \int_0^l \frac{\partial \varphi_i^\phi}{\partial x} \frac{\partial \varphi_j^{Li^+}}{\partial x} dx c_j^{Li^+} + \\ &D_{X^-} \int_0^l \frac{\partial \varphi_i^\phi}{\partial x} \frac{\partial \varphi_k^\phi}{\partial x} \varphi_j^{X^-} dx c_j^{X^-} \phi_k - D_{X^-} \int_0^l \frac{\partial \varphi_i^\phi}{\partial x} \frac{\partial \varphi_j^{X^-}}{\partial x} dx c_j^{X^-} \\ \frac{f_i^*(t)}{RT c_{bulk}} &= \frac{1}{c_{bulk}} \int_{\partial N_V} (\varphi_i^\phi + \varphi_i^{Li^+}) h_{BV} d\Gamma \end{aligned}$$

$$h_{BV}|_{(x=0)}(t) = h_{BV}|_{(x=l)}(t) = -\frac{I(t)}{FA} \quad (36a)$$

$$\vec{h}_{X^-} \cdot \vec{n}|_{(x=0)}(t) = \vec{h}_{X^-} \cdot \vec{n}|_{(x=l)}(t) = 0 \quad (36b)$$

- see also Fig. 1. From identity (35), the “steady” mass flux at $t \gg 0$

¹⁰ As in Section 7 of [1] the star superscript is omitted from the definition of dimensionless quantities for the sake of readability: for example, in this section $c_j^{Li^+}$ stands for the j -th nodal unknown for Li -ions dimensionless concentration at time t . Furthermore, the usual Einstein summation convention is applied henceforth: when an index variable appears twice in a single term it implies summation of that term over all the values of the index.

The non linear form $a_i^* \text{sat}[y(t)]$ on the contrary, contains the saturation contributions (not accounted for in Ref. [1]). It reads

As in Ref. [1], a Newton–Raphson scheme has been implemented to solve the non-linear problem (38).

$$\begin{aligned} \frac{\text{sat} a_i^*[y(t)]}{RT c_{\text{bulk}}} = & \mathbb{D}_{\text{Li}^+} \int_0^l \varphi_j^{\text{Li}^+} c_j^{\text{Li}^+} \left(-\frac{2}{c_{\text{max}}} \varphi_n^{\text{Li}^+} c_n^{\text{Li}^+} \right) \frac{\partial \varphi_i^{\text{Li}^+}}{\partial x} \frac{\partial \varphi_k^{\phi}}{\partial x} \phi_k dx + \\ & + \mathbb{D}_{\text{Li}^+} \int_0^l \varphi_j^{\text{Li}^+} c_j^{\text{Li}^+} \left(-\frac{2}{c_{\text{max}}} \varphi_n^{\text{Li}^+} c_n^{\text{Li}^+} \right) \frac{\partial \varphi_i^{\phi}}{\partial x} \frac{\partial \varphi_k^{\phi}}{\partial x} \phi_k dx + \\ & - \mathbb{D}_{\text{X}^-} \int_0^l \varphi_j^{\text{X}^-} c_j^{\text{X}^-} \left(-\frac{2}{c_{\text{max}}} \varphi_n^{\text{X}^-} c_n^{\text{X}^-} \right) \frac{\partial \varphi_i^{\text{X}^-}}{\partial x} \frac{\partial \varphi_k^{\phi}}{\partial x} \phi_k dx + \\ & + \mathbb{D}_{\text{X}^-} \int_0^l \varphi_j^{\text{X}^-} c_j^{\text{X}^-} \left(-\frac{2}{c_{\text{max}}} \varphi_n^{\text{X}^-} c_n^{\text{X}^-} \right) \frac{\partial \varphi_i^{\phi}}{\partial x} \frac{\partial \varphi_k^{\phi}}{\partial x} \phi_k dx \end{aligned}$$

A family of time-advancing methods based on the so-called θ -scheme can be set up for the discrete problem (37). In the numerical simulations that follows, the backward Euler scheme ($\theta=1$) has been selected, thus seeking for $y(t+\Delta t)$ such that

$$\begin{aligned} b_i^* \frac{y(t+\Delta t)}{\Delta t} + a_i^* \cdot y(t+\Delta t) + \text{sat} a_i^*[y(t+\Delta t)] \\ = f_i^*(t+\Delta t) + b_i^* \cdot \frac{y(t)}{\Delta t} \end{aligned} \quad (38)$$

7.3. Simulations

Charge process simulations have been carried out with different C-rates. An anti-symmetric ionic concentration profile arises in the electrolyte, initiated at the bulk concentration c_{bulk} that reflects thermodynamic equilibrium at time $t=0$. Such a feature, emerged in Ref. [1] at a unit C-rate, is clearly envisaged also at different charging speeds, as emphasized in Fig. 2. Either when C-rates are high (say 2 or more), or when the charge duration allows to reach a steady-state configuration at moderate C-rates (say about 1), the

Fig. 4. Evolution in time of the difference $\Delta\phi(x,t)=\phi(x,t)-\phi_{\text{nosat}}(x,t)$ for several C-rates. The trend of the evolution in time is also depicted.

Fig. 5. Evolution in time of the ratio $\Delta\phi(x, t) \times \phi_{nosat}^{-1}(x, t)$ for several C-rates. The trend of the evolution in time is also depicted.

concentration near the electrodes are close to the limit concentration $c_{Li^+} = 0$ at one side and close to the symmetric concentration $c_{Li^+} = 2c_{bulk}$ at the other electrode. The latter concentration is higher than half of the saturation limit of the Li salt in the electrolyte solvent.

Several numerical analyses were performed to investigate the influence of spatial and temporal discretization. The results for 150 equal finite elements and a constant time step of 1 s are here given. At the initial time the electric potential follows equation (31) and has to be homogeneous for thermodynamic equilibrium with no current nor mass flow.

$$\phi(\vec{x}, 0) = 0 \quad \vec{x} \in V \quad (39)$$

After a “sufficiently long” time, the steady state configuration has been approximated at C-rates less than 2. Analyses at higher C-rates end prematurely before achieving the steady state configuration, because the limit concentration $c_{Li^+} = 0$ was approached at the Anode. As a chosen small lower bound, discharge process simulations have been arrested at 1% of initial concentration. In particular, for C-rate = 2 the final time was $t_f = 210$ s, whereas for C-rate = 4 the analyses have been terminated at $t_f = 54$ s. Concentration profiles in the presence of saturation at different C-rates are represented in Fig. 2-d. The upper part of the figure, which is shadowed, refers to the Cathode, where concentration of Li^+ ions increase during charge processes. The lowest part refers to the

Anode. The concentration profiles are symmetric with respect to the bulk concentration $c_{bulk} = 1500 \text{ mol m}^{-3}$. As shown in Ref. [1] for a unit C-rate, the steady state asymptotic behavior is recovered well, but steady state concentrations have not been represented to the sake of readability.

Fig. 2-e assesses the electroneutrality condition (1), which is well approximated by the numerical solution, in the sense that the difference in concentration is about nine to ten orders of magnitude smaller than the equilibrium electrolyte concentration c_{bulk} .

Denote with $c_{Li^+}^{nosat}(x, t)$ the solution for the Li-ions concentration under the assumption far from saturation – i.e. assuming $c^{max} \rightarrow \infty$ in governing equation (27) – and with $c_{Li^+}(x, t)$ the solution for the Li-ions concentration of governing equation (27) with $c^{max} = 10^4 \text{ mol m}^{-3}$. Fig. 2-f depicts the absolute difference in concentration $\Delta c(x, t)$ between the solutions with and without saturation

$$\Delta c(x, t) = |c_{Li^+}(x, t) - c_{Li^+}^{nosat}(x, t)|$$

along the electrolyte $0 \leq x \leq 0.28 \text{ mm}$ for a galvanostatic process at a unit C-rate. Similar profiles result for other C-rates. The difference ranges between $10^{-15} < \Delta c(x, t) < 10^{-12} \text{ mol m}^{-3}$ depending on time $0 \leq t \leq t_f = 1000$ s. It can be assessed from Fig. 2 that ionic concentrations are in the order of 10^3 mol m^{-3} along the electrolyte in the whole time frame. Accordingly, the influence of the saturation on concentrations is negligible. This effect is attributed to

Fig. 6. Buildup of internally generated entropy for Li^+ (continuous curve) and for PF_6^- (dashed curve) at different C-rates in the presence of saturation.

electroneutrality.

As the deviation from electroneutrality is small, see again Fig. 2-e, the analysis that follows provides an acceptable rationale to the observed independence of ionic concentrations upon saturation. Consider mass balance equations (27a) and (27b), here rewritten when electroneutrality (1) applies¹¹

$$\frac{\partial c}{\partial t} + \text{div} \left[-D_{\text{Li}^+} \nabla [c] - F \psi_{\text{Li}^+} c \left(1 - 2 \frac{c}{c^{\max}} \right) \nabla [\phi] \right] = 0 \quad (40a)$$

$$\frac{\partial c}{\partial t} + \text{div} \left[-D_{\text{X}^-} \nabla [c] + F \psi_{\text{X}^-} c \left(1 - 2 \frac{c}{c^{\max}} \right) \nabla [\phi] \right] = 0 \quad (40b)$$

By multiplying the Li^+ balance equation with the ion mobility ψ_{X^-} and the X^- balance equation with the ion mobility ψ_{Li^+} the two equation (40) can be added, leading to

$$(\psi_{\text{X}^-} + \psi_{\text{Li}^+}) \frac{\partial c}{\partial t} - 2RT (\psi_{\text{X}^-} * \psi_{\text{Li}^+}) \Delta [c] = 0 \quad (41)$$

Ionic concentrations in the assumption of electroneutrality are therefore independent upon $c^{\max}$. Indeed, equation (41) can be

derived without taking into account the saturation in Fick's law (25).

Denote with $\phi_{\text{nosat}}(x, t)$ the solution for the electric potential when concentrations are far from saturation – i.e. assuming $c^{\max} \rightarrow \infty$ in governing equation (27) – and with $\phi(x, t)$ the solution for the electric potential of governing equation (27) with $c^{\max} = 10000 \text{ mol m}^{-3}$. Electric potential profiles at the Cathode in the presence of saturation or without saturation at different C-rates are represented in Fig. 3.

Fig. 4 depicts the evolution in time of the difference

$$\Delta \phi(x, t) = \phi(x, t) - \phi_{\text{nosat}}(x, t)$$

in the electric potential $\phi(x)$. The picture clearly shows that saturation does influence the electric potential and that the difference increases with time for all C-rates. Having set the potential to be zero at the anode, this conclusion was theoretically predicted in Section 5, since saturation constitutively affects the electric contribution in the mass flux (25) by changing the mobility, thus creating a higher potential gradient in galvanostatic processes.

The relative difference

$$\Delta \phi(x, t) \times \phi_{\text{nosat}}^{-1}(x, t)$$

is plotted in Fig. 5. The latter shows that the saturation increases the electric potential by about 40% near the cathode for all C-rates. This

¹¹ implying $c_{\text{Li}^+} = c_{\text{X}^-} = c$

Fig. 7. Total internal entropy production (43) with (continuous curve) and without (dashed curve) saturation.

effect appears to be more pronounced at small C-rates, when concentrations may not be as close to the saturation limit at the end of the analysis t_f as they are for high C-rates.

According to the Clausius-Planck inequality, the Internal Entropy Production (shortened in IEP) cannot be negative. Following the approach of rational thermodynamics of Coleman and Noll, it can be written as:

$$IEP(x, t) = -\frac{1}{T} \sum_{\alpha} \vec{h}_{\alpha} \cdot \nabla [\bar{\mu}_{\alpha}] \geq 0 \quad (42)$$

for isothermal processes with no inelastic mechanical effects. Substituting Fick's law (20) and the mobility (22) in (42), the total internal entropy production equals

$$\frac{1}{T} \sum_{\alpha} \int_0^{t_f} \int_0^L \frac{1}{\psi_{\alpha} c_{\alpha} (1 - 2 \frac{c_{\alpha}}{c_{\alpha}^{max}})} \vec{h}_{\alpha} \cdot \vec{h}_{\alpha} dx dt \quad (43)$$

with $\vec{h}_{\alpha}$ as in equation (25). Integration over time can be approximated in every time step by means of a trapezoidal rule. Furthermore, having used linear shape functions to approximate the concentration and potential fields, gradients are constant in each finite element. The scalar product $\vec{h}_{\alpha} \cdot \vec{h}_{\alpha}$ turns out to be a polynomial of degree four in the space variable x , which is trivially integrated. The integral

$$\frac{1}{T} \int_0^t \int_0^L \frac{1}{u_{\alpha} c_{\alpha} (1 - 2 \frac{c_{\alpha}}{c_{\alpha}^{max}})} \vec{h}_{\alpha} \cdot \vec{h}_{\alpha} dx d\tau \quad (44)$$

is plotted in Fig. 6 as a function of time t . It represents the buildup of internally generated entropy for Li^+ (continuous curve) and for PF_6^- (dashed curve), respectively, at different C-rates in the presence of saturation. At low C-rates, the flux of ions PF_6^- abates with time (see Fig. 5 in Ref. [1]) and the slope of the IEP gets flatter and flatter with time.¹² Similarly, the flux of ions Li^+ tends to a constant while approaching the steady state conditions. The two effects combined induce a linear trend with time for the IEP at low C-rates. A similar behavior would be expected at higher C-rates, but the limit concentration is reached well before the steady state configuration.

Fig. 7 compares the total IEP (43) with and without saturation. The increment of internally generated entropy due to the saturation

¹² The flux near the electrode interfaces is dictated by the boundary conditions. The closer the regions to the electrodes the faster they reach the steady state – see Fig. 5 in Ref. [1]. As discussed in Ref. [2] the Li^+ ionic current is mainly carried by migration at the beginning of the charging process, while under steady-state conditions diffusion and migrations contribute equally. The anionic mass flux reaches its peak rapidly, and once the steady state is approached, the flux of PF_6^- tends to vanish, and no contribution is provided further to the overall ionic conductivity.

Fig. 8. The effect of the saturation within the free energy density favors the diffusion into the electrolyte and reduces the concentration gradient at the electrodes.

is in the order of 40% of the unsaturated electrolyte IEP. The higher the C-rate the higher the rate of internally generated entropy. Nevertheless, as the limit concentration is reached at high charge rates, one cannot conclude that the total accumulation of IEP is larger at high C-rates.

8. Conclusions

In a recent paper [1], ionic conductivity was modeled with the final aim of using computational simulations as a predictive tool in energy storage electrochemistry. A novel formulation was proposed, stemming from Maxwell's equations in their electro-quasi-static form instead of the classical condition of electroneutrality. From the thermodynamic standpoint, ideal solutions far from saturation were used underlying the constitutive theory for diffusion and migration processes. As shown in Section 7.3, ionic concentrations in real batteries can be higher than half of the saturation limit of the Li salt in the electrolyte solvent. Accordingly, the assumption of ideal solutions far from saturation can be questioned.

The present study investigated this assumption, for the case where concentrations are too high to neglect the role of saturation but still sufficiently low to exclude incomplete dissociation of the Li-salt. This conjecture is confirmed by the data and the numerical simulations on real batteries.

The adopted constitutive specifications (25) account for the saturation contribution. By comparing it with the mass flux constitutive equation adopted in Refs. [1], here reprinted in formula (26), one notices that saturation has no effect on the diffusivity. Under the assumption of electroneutrality, it can be assessed that saturation does not impact the concentration profiles either. In fact, the electroneutrality condition (1) is well approximated during the simulations and the influence of saturation on the concentration profiles is actually negligible – see Fig. 2-e.

Saturation does however affect the electric potential in view of the mass flux equation (25) because it modifies the ionic mobility, inducing a higher potential gradient as shown in the simulations. Figs. 4 and 5 confirm that the saturation may increase the electric potential by about 40% near the cathode for all C-rates. Saturation influences the internal entropy production to a similar extent, as conveyed in Figs. 6 and 7.

In conclusion, saturation appears to be an essential ingredient in a multi scale and multi physics approach for battery modeling

[16,15]. Furthermore, the fully three-dimensional formulation that was proposed in Ref. [1] and the numerical algorithms that emanate from the weak form established therein have shown to be robust and capable of incorporating the new constitutive specifications, as required to account for the saturation.

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Nomenclature

Notation

Vectors $\vec{a}$ will be denoted by an over-right-arrow, second order tensors $\mathbf{A}$ by bold face. This notation does not apply to operators.

Operators

- the symbol $\text{div}[-]$ denotes the divergence operator
- the symbol $\nabla[-]$ denotes the gradient operator
- the symbol $\text{curl}[-]$ denotes the curl operator
- the symbol $\Delta[-]$ denotes the Laplace operator
- the symbol $\cdot$ denotes the single contraction of two vectors or two tensors
- the symbol $:$ denotes the double contraction of two tensors
- the symbol $\|\vec{x}\|^2$ denotes the squared norm of vector $\vec{x}$ or tensor $\mathbf{x}$

Subscripts and superscripts

- the subscript Li^+ identifies quantities for Lithium cations, at both scales
- the subscript X^- identifies quantities for anions, at both scales

Variables and fields

Electromagnetic variables and fields

- $\vec{B}$ denotes magnetic field [T]
- $\vec{D}$ denotes electric displacement field [C m^{-2}]
- $\vec{E}$ denotes electric field [V m^{-1}]
- $\vec{H}$ denotes magnetizing field [A m^{-1}]
- $\vec{i}$ denotes the electric current density [A m^{-2}]
- ϵ denotes the permittivity [F m^{-1}]
- ζ denotes the charge density [C m^{-3}]
- ϕ denotes the electric potential [V]

Mass transport variables and fields

- c denotes the concentration measure called molarity [mol m^{-3}]
- $\vec{h}_\alpha$ denotes the mass flux of species α [$\text{mol m}^{-2} \text{s}^{-1}$]
- z_α denotes the valency of ion α [-]

- μ denotes the chemical potential, also known as partial molar free energy [J mol⁻¹]
- $\bar{\mu}$ denotes the electrochemical potential [J mol⁻¹]
- μ denotes the permeability [N A⁻²]

Geometrical variables and fields

- $\vec{n}$ denotes the outward normal direction on a surface
- V denotes a domain
- ∂V denotes a boundary or an interface between domains

Other variables and fields

- t denotes time [s]
- T denotes the absolute temperature [K]
- $\vec{q}$ denotes the heat flux vector [W m⁻²]
- s_q denotes the heat supply [W m⁻³]

Constants and parameters

- N_A is Avogadro's number, $N_A = 6.02214129(27) \times 10^{23}$ mol⁻¹
- e is elementary charge, $e = 1.602176565(35) \times 10^{-19}$ C
- $F = N_A e$ is Faraday's constant, $F = 96485.3383$ C mol⁻¹
- R is the universal gas constant 8.3144621 J K⁻¹ mol⁻¹
- ϵ_0 is the vacuum permittivity, $8.85418782 \times 10^{-12}$ F m⁻¹

Appendix A. Thermodynamics

A.1 First law

The balance between the internal energy ($\mathcal{U}$) of a material region $\mathcal{P}$, the mechanical external power ($\mathcal{W}$) expended on $\mathcal{P}$, the heat transferred ($\mathcal{Q}$) in $\mathcal{P}$, and the power due to mass ($\mathcal{T}$) and electromagnetic ($\mathcal{E}$) interactions exchanged on $\mathcal{P}$ for the problem at hand, for *quasi-static interactions*, reads:

$$\frac{\partial \mathcal{U}}{\partial t}(\mathcal{P}) = \mathcal{W}(\mathcal{P}) + \mathcal{Q}(\mathcal{P}) + \mathcal{T}(\mathcal{P}) + \mathcal{E}(\mathcal{P}) \quad (45)$$

It is assumed that these processes occur with *their distinctive contributions* in the balance, in particular *the energies due to charges and mass transfer are additively treated* as two separate processes. The individual contributions are: i) a mechanical contribution due to body forces $\vec{b}$ and surface forces $\vec{p}$ that spend power against velocities $\vec{v}$;

$$\mathcal{W}(\mathcal{P}) = \int_{\mathcal{P}} \vec{b} \cdot \vec{v} d\Omega + \int_{\partial \mathcal{P}} \vec{p} \cdot \vec{v} d\Gamma \quad (46a)$$

ii) a heat contribution where the scalar s_q is the heat supplied by external sources and $\vec{q}$ is the heat flux vector;

$$\mathcal{Q}(\mathcal{P}) = \int_{\mathcal{P}} s_q d\Omega - \int_{\partial \mathcal{P}} \vec{q} \cdot \vec{n} d\Gamma \quad (46b)$$

iii) a mass flux contribution with the scalar μ denoting the chemical potential, the scalar s_α the supply of species ($\alpha = \text{Li}^+, \text{X}^-$) and $\vec{h}_\alpha$ the mass flux vector;

$$\mathcal{T}(\mathcal{P}) = \sum_{\alpha} \left\{ \int_{\mathcal{P}} \mu_{\alpha} s_{\alpha} d\Omega - \int_{\partial \mathcal{P}} \mu_{\alpha} \vec{h}_{\alpha} \cdot \vec{n} d\Gamma \right\} \quad (46c)$$

iv) an electromagnetic contribution with the energy flux vector

$\vec{E} \times \vec{H}$ generated by the electric and magnetizing fields.¹³

$$\mathcal{E}(\mathcal{P}) = - \int_{\partial \mathcal{P}} (\vec{E} \times \vec{H}) \cdot \vec{n} d\Gamma \quad (46d)$$

A specific (per unit volume in the reference body, see Ref. [9]) internal energy u is usually defined as

$$\mathcal{U}(\mathcal{P}) = \int_{\mathcal{P}} u d\Omega$$

in order to write the local form of the first principle. Standard application of the divergence theorem and of mass balances (2) leads from (46) to

$$\mathcal{W}(\mathcal{P}) = \int_{\mathcal{P}} \sigma : \frac{\partial \epsilon}{\partial t} d\Omega \quad (47a)$$

$$\mathcal{Q}(\mathcal{P}) = \int_{\mathcal{P}} s_q - \text{div} [\vec{q}] d\Omega \quad (47b)$$

$$\mathcal{T}(\mathcal{P}) = \sum_{\alpha} \int_{\mathcal{P}} \mu_{\alpha} \frac{\partial c_{\alpha}}{\partial t} - \vec{h}_{\alpha} \cdot \nabla [\mu_{\alpha}] d\Omega \quad (47c)$$

$$\mathcal{E}(\mathcal{P}) = \int_{\mathcal{P}} \left(\frac{\partial \vec{D}}{\partial t} + \vec{i} \right) \cdot \vec{E} d\Omega \quad (47d)$$

The electromagnetic contribution (47d) comes out under the assumption of electro-quasi-statics and in view of Ampère's-Maxwell's law (9). Since the energy balance (45) must hold for all regions $\mathcal{P}$, the global energy balance (45) can be written in a so-called "local form" at any point $\vec{x} \in \mathcal{P}$

$$\frac{\partial u}{\partial t} = \sigma : \frac{\partial \epsilon}{\partial t} + s_q - \text{div} [\vec{q}] + \left(\frac{\partial \vec{D}}{\partial t} + \vec{i} \right) \cdot \vec{E} + \sum_{\alpha} \mu_{\alpha} \frac{\partial c_{\alpha}}{\partial t} - \vec{h}_{\alpha} \cdot \nabla [\mu_{\alpha}] \quad (48)$$

The electromagnetic contribution (47) to the energy balance can be given a different expression in the framework of electro-quasi-statics, keeping in mind that charges are conveyed together with mass and thus the processes of migration and diffusion are coupled. The link between the two processes is Faraday's laws of electrolysis (4). Exploiting them and Gauss's law (5), (47) becomes

¹³ $\vec{E} \times \vec{H}$ is an energy flux vector results from Poynting's theorem (see also [10,11]). $\mathcal{E}(\mathcal{P}) = - \int_{\mathcal{P}} (\vec{E} \times \vec{H}) \cdot \vec{n} d\Gamma = - \int \text{div} [\vec{E} \times \vec{H}] d\Omega = \int \vec{H} \cdot \text{curl} [\vec{E}] - \text{curl} [\vec{H}] \cdot \vec{E} d\Omega$ After substitution of the curls from Maxwell's equations, Poynting's theorem results.

$$\begin{aligned}
\mathcal{E}(\mathcal{P}) &= - \int_{\mathcal{P}} \frac{\partial \vec{D}}{\partial t} \cdot \nabla[\phi] + \vec{i} \cdot \nabla[\phi] d\Omega \\
&= - \int_{\mathcal{P}} \operatorname{div} \left[\phi \frac{\partial \vec{D}}{\partial t} \right] - \phi \operatorname{div} \left[\frac{\partial \vec{D}}{\partial t} \right] + F \sum_{\alpha} z_{\alpha} \vec{h}_{\alpha} \cdot \nabla[\phi] d\Omega \\
&= \int_{\mathcal{P}} \phi \frac{\partial \zeta}{\partial t} - \sum_{\alpha} (F z_{\alpha} \nabla[\phi]) \cdot \vec{h}_{\alpha} d\Omega - \int_{\partial \mathcal{P}} \phi \frac{\partial \vec{D}}{\partial t} \cdot \vec{n} d\Gamma \\
&= \sum_{\alpha} \int_{\mathcal{P}} (F z_{\alpha} \phi) \frac{\partial c_{\alpha}}{\partial t} - (F z_{\alpha} \nabla[\phi]) \cdot \vec{h}_{\alpha} d\Omega - \int_{\partial \mathcal{P}} \phi \frac{\partial \vec{D}}{\partial t} \cdot \vec{n} d\Gamma
\end{aligned} \quad (49)$$

From (47, 49), the power expenditure due to mass transfer and electromagnetic interactions specialize in the electrolyte as:

$$\begin{aligned}
\mathcal{T}(\mathcal{P}) + \mathcal{E}(\mathcal{P}) &= \sum_{\alpha} \int_{\mathcal{P}} (\mu_{\alpha} + F z_{\alpha} \phi) \frac{\partial c_{\alpha}}{\partial t} - \vec{h}_{\alpha} \cdot \nabla[\mu_{\alpha} + F z_{\alpha} \phi] d\Omega \\
&\quad - \int_{\partial \mathcal{P}} \phi \frac{\partial \vec{D}}{\partial t} \cdot \vec{n} d\Gamma
\end{aligned} \quad (50)$$

In the absence of charged species, only diffusion takes place; the relevant constitutive theory can be found in Refs. [9], section 66. In its dual way, in the absence of gradients of chemical potential, diffusion cannot proceed and current is thus driven by migration only. When diffusion is present, a current density appears due to Faraday's law and both processes contribute to the charge flux. It is therefore clear that concentration gradients and electric field act contemporarily to generate ion mobility. This is the intimate nature of the energy contribution (50) and of the electrochemical potential $\bar{\mu}_{\alpha}$ that in light of (50) will be defined by the decomposition

$$\bar{\mu}_{\alpha} = \mu_{\alpha} + F z_{\alpha} \phi \quad (51)$$

- see also [11], chapter XIII, Section 3.4, formula (42). Accordingly, the local form of the first principle in terms of rates of the referential internal energy u reads also:

$$\frac{\partial u}{\partial t} = \sigma : \frac{\partial \epsilon}{\partial t} + s_q - \operatorname{div} [\vec{q}] - \operatorname{div} \left[\phi \frac{\partial \vec{D}}{\partial t} \right] + \sum_{\alpha} \bar{\mu}_{\alpha} \frac{\partial c_{\alpha}}{\partial t} - \vec{h}_{\alpha} \cdot \nabla[\bar{\mu}_{\alpha}] \quad (52)$$

The internal energy u is written as a function of the state variables, namely the entropy η , the concentrations c_{α} , the electric displacement field $\vec{D}$, and the kinematic variables in terms of the small strain tensor ϵ , i.e.

$$\frac{\partial u}{\partial t} = \frac{\partial u}{\partial \eta} \frac{\partial \eta}{\partial t} + \frac{\partial u}{\partial \epsilon} : \frac{\partial \epsilon}{\partial t} + \frac{\partial u}{\partial \vec{D}} \cdot \frac{\partial \vec{D}}{\partial t} + \sum_{\alpha} \frac{\partial u}{\partial c_{\alpha}} \frac{\partial c_{\alpha}}{\partial t} \quad (53)$$

A.2 Second law

A local form of the entropy imbalance can be derived from the Clausius-Duhem inequality in terms of the referential entropy η and of the absolute temperature T [9]:

$$\frac{\partial \eta}{\partial t} - \frac{s_q}{T} + \operatorname{div} \left[\frac{\vec{q}}{T} \right] \geq 0 \quad (54)$$

By noting that

$$\operatorname{div} \left[\frac{\vec{q}}{T} \right] = \frac{1}{T} \operatorname{div} [\vec{q}] - \frac{1}{T^2} \vec{q} \cdot \nabla[T]$$

equation (54) can be expressed in terms of internal energy, exploiting equations (48) and (53). The entropy imbalance yields

$$\begin{aligned}
&\frac{\partial \eta}{\partial t} \left(T - \frac{\partial u}{\partial \eta} \right) + \frac{\partial \epsilon}{\partial t} : \left(\sigma - \frac{\partial u}{\partial \epsilon} \right) + \frac{\partial \vec{D}}{\partial t} \cdot \left(\vec{E} - \frac{\partial u}{\partial \vec{D}} \right) \\
&+ \sum_{\alpha} \frac{\partial c_{\alpha}}{\partial t} \left(\mu_{\alpha} - \frac{\partial u}{\partial c_{\alpha}} \right) + \vec{i} \cdot \vec{E} - \sum_{\alpha} \vec{h}_{\alpha} \cdot \nabla[\mu_{\alpha}] - \frac{1}{T} \vec{q} \cdot \nabla[T] \geq 0
\end{aligned} \quad (55)$$

Term $\vec{i} \cdot \vec{E}$ is the Joule effect. In view of Faraday's law, straightforward algebra allows to write:

$$\vec{i} \cdot \vec{E} - \sum_{\alpha} \vec{h}_{\alpha} \cdot \nabla[\mu_{\alpha}] = - \sum_{\alpha} \vec{h}_{\alpha} \cdot \nabla[\bar{\mu}_{\alpha}]$$

taking into account (51). By applying the Coleman-Noll procedure, inequality (55) must hold for all constitutive processes [9,19], giving rise to the following thermodynamic restrictions:

$$\begin{aligned}
T - \frac{\partial u}{\partial \eta} &= 0, \quad \sigma - \frac{\partial u}{\partial \epsilon} = 0, \quad \mu_{\alpha} - \frac{\partial u}{\partial c_{\alpha}} = 0, \quad \vec{E} - \frac{\partial u}{\partial \vec{D}} = 0, \\
\vec{h}_{\alpha} \cdot \nabla[\bar{\mu}_{\alpha}] &\leq 0, \quad \frac{1}{T} \vec{q} \cdot \nabla[T] \leq 0
\end{aligned} \quad (56)$$

Different thermodynamic potentials can be considered rather than the internal energy u . A classical one is the specific *Helmholtz free energy*

$$\psi(T, \epsilon, c_{\alpha}, \vec{E}) = u(\eta, \epsilon, c_{\alpha}, \vec{D}) - T\eta - \vec{E} \cdot \vec{D}$$

that will be used henceforth in the assumption of processes in thermal equilibrium. Thermodynamic restrictions then read:

$$\begin{aligned}
\sigma - \frac{\partial \psi}{\partial \epsilon} &= 0, \quad \mu_{\alpha} - \frac{\partial \psi}{\partial c_{\alpha}} = 0, \quad \vec{D} + \frac{\partial \psi}{\partial \vec{E}} = 0, \quad \vec{h}_{\alpha} \cdot \nabla[\bar{\mu}_{\alpha}] \leq 0, \\
\frac{1}{T} \vec{q} \cdot \nabla[T] &\leq 0
\end{aligned} \quad (57)$$

Appendix B. Concentrated solutions

According to Ficks law (20) there is no influence of other phases on the flux of species α , i.e. cross-effects are ignored although they may appear in reality. To account for interactions between phases, the standard approach [20] 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:

$$\vec{h}_{\alpha} = - \sum_{\beta=1}^2 \mathbf{M}_{\alpha\beta}(c_1, c_2) \nabla[\bar{\mu}_{\beta}] \quad \alpha = 1, 2 \quad (58)$$

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

$$\mathbf{M}_{\alpha\beta}(c_1, c_2) = M_{\alpha\beta}(c_1, c_2) c_{\alpha} \mathbf{1}$$

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 (4) and symmetric due to the Onsager reciprocal relations. The approach that provides specifications for $M_{\alpha\beta}$ is usually known as the Maxwell–Stefan approach [21].

Appendix C. Steady state solutions

The porous electrode theory developed by Newman and co-workers [13] stems from the mass balance equation (3) and from electroneutrality condition

$$c_{\text{Li}^+} = c_{\text{X}^-} = c$$

It is straightforward to derive equation (41) which is independent of the electric potential, even in the case of saturation as modeled via Fick's law (25). At steady state, the laplacian vanishes thus leading to a linear form $c_{\infty}(x)=ax+b$ for the concentration in 1D problems. The two parameters a and b can be determined by imposing the galvanostatic flux h_{1C} at $x=0$ and by imposing the mass conservation through time, namely

$$\int_0^l c(x, t) dx = \int_0^l c(x, 0) dx$$

which at steady state leads to

$$a \frac{l^2}{2} + b l = c_{\text{bulk}} l$$

and finally to the steady state concentration

$$c_{\infty}(x) = c_{\text{bulk}} - \frac{h_{1C}}{2D_{\text{Li}^+}} \left(x - \frac{l}{2} \right) \quad (59)$$

The steady state solution is useful to envisage the role played by the non linear mobility tensor and by the free energy density at saturation in Fick's law (25). If one, for instance, takes the linear isotropic mobility tensor

$$M_{\alpha}(c_{\alpha}) = \psi_{\alpha} c_{\alpha} \mathbb{1} \quad (60)$$

together with the ideal solution model (5), the mass balance equation (41) restated in 1D reads:

$$(\psi_{\text{X}^-} + \psi_{\text{Li}^+}) \frac{\partial c}{\partial t} - 2RT \psi_{\text{X}^-} \psi_{\text{Li}^+} \{ f(c) \Delta [c] + f'(c) (c'(x))^2 \} = 0 \quad (61)$$

having defined

$$f(c) = 1 + \frac{c}{c^{\text{max}}} \frac{2}{1 - 2 \frac{c}{c^{\text{max}}}}$$

At steady state, one is left with a non linear ordinary differential equation

$$f(c) \Delta [c] + f'(c) (c'(x))^2 = 0$$

which admits the following solution:

$$c_{\infty}(x) = \frac{e^{2a(b+x)} + ac^{\text{max}}}{2a}$$

with parameters a and b to be evaluated again by imposing the galvanostatic flux h_{1C} at $x=0$ and by imposing the mass conservation through time. The effect of the saturation within the free energy density is clearly envisaged in Fig. 8. It corresponds to a higher diffusivity, in turn dependent upon the concentration, which favors the diffusion into the electrolyte and decreases both the concentration at the electrodes and the concentration gradient within the electrolyte. On the contrary, the non linear isotropic mobility tensor itself causes a decrease of the diffusivity, with opposite effects. Indeed, they cancel out in the final Fick's law (25).

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