



A multiscale-compatible approach 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.
- Multiphysics coupling is fully 3D, 2D simulations are performed.
- Microstructural and stress analysis are made possible by the present formulation.

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ABSTRACT

A novel approach in modeling the ionic transport in the electrolyte of Li-ion batteries is here presented. Diffusion and migration processes govern the transport of ions in solution in the absence of convection. In the porous electrode theory [1] it is common to model these processes via mass balance equations and electroneutrality. A parabolic set of equations arises, in terms of a non constant electric field which is afflicted by the paradox of being generated without electrical charges. To remedy this contradiction, Maxwell's equations have been used here, coupled to Faraday's law of electrochemical charge transfer. The set of continuity equations for mass and Maxwell's equations lead to a consistent model, with distinctive energy characteristics. Numerical examples show the robustness of the approach, which is well suited for multi-scale analyses [2,3].

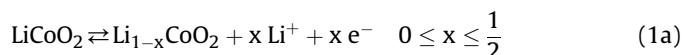
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1. Introduction

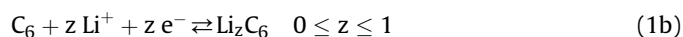
An electrochemical cell incorporates two electrodes, a separator, and an electrolytic solution – see Fig. 1. Li-ions are extracted from the cathode (positive electrode) during charging and inserted back during discharging. The opposite holds for the anode (negative electrode). Assuming LiCoO₂ to be the positive electrode material for instance, the following electrochemical charge transfer reaction holds.

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If graphite is taken to serve as the negative electrode material, intercalation and extraction are described by



The inter-electrode medium is a multi-phase composite structure, liquid electrolyte plus separator, that includes a network of interconnected and irregular pores [4]. Separators have to be designed to prevent internal short circuiting while providing a path for ionic conduction in the liquid electrolyte throughout its open porous structure. They are usually classified in microporous polymer membranes, non-woven fabric mats and inorganic composite

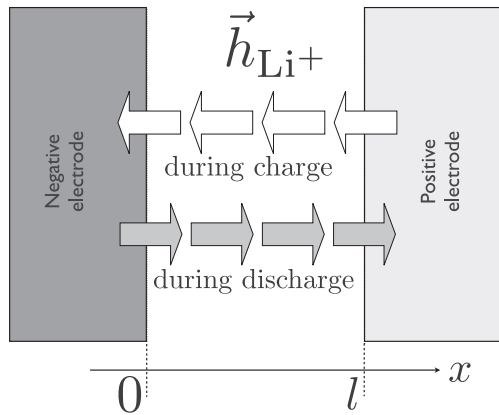


Fig. 1. A one-dimensional scheme of a Li-ion battery. The flux of Li^+ ions during charge/discharge is highlighted. The notation that will be used in one dimensional simulations in section 7 is also pointed out.

membranes (recent reviews can be found in Refs. [5,6]). Although the separator does not participate in the electrochemical reaction it influences the performance of Li-ion battery cells, as experimentally observed by *Djian et al.* [7].

Mobile species in the electrolyte are therefore ions and predicting the behavior of electrochemical cells requires quantitative modeling of the kinetics of mobile ionic species, which is influenced by the affinity between separator and electrolyte, geometry, orientation, mean size and interconnection of the pores.

At a macroscopic scale, geometrical aspects are resumed through global geometric parameters: *porosity* and *tortuosity*. The former quantifies volume fraction occupied by the pores; the identification of an *optimal* value is a compromise between the minimization of the ionic resistance, enabling high-specific battery power (high porosity and large mean pore size), and the limitations dictated by the mechanical resistance of the membrane, preventing the risk of inner battery electrical shorting (thick membrane and low porosity). The tortuosity is a measure of how the conductive pathways deviate from an ideal condition of straight channel of uniform cross section [4]. Increasing tortuosity also increases the mean path length of ions [6], thus favouring unwanted effects.

Many attempts can be found in the literature, [4,8–11] among others, to relate porosity and tortuosity to effective *conductivity* and *diffusivity* of inhomogeneous media. The influence of the underlying microstructure on to macroscopic material properties is the goal of homogenization theory and recent publications have been devoted to computational homogenization for Li-ion batteries [2,3].

Lithium is transported through the separator from one electrode to the other, to bring reactants to the interfaces for the electrochemical charge transfer reactions (1) to take place. Diffusion is governed by transport of mass, which is a conserved quantity, and described by the mass continuity equation, which is linked to the two ionic concentrations c_{Li^+} and c_{X^-} and to the mass fluxes of Li^+ and X^- . Nevertheless, the set of two mass balance equations contains a further unknown, the electric field, because ionic transport entails movement of mass as well as of charge. For that reason, coupling with an additional relation is mandatory, to model the migration process.

The most common selection for such an additional relation in battery modeling is the *electroneutrality* condition

$$c_{\text{Li}^+} - c_{\text{X}^-} = 0 \quad (2)$$

In several studies, originated by Newman [1] and collectively gathered in the terminology “porous electrode theory”, condition (2) is used *in lieu of Maxwell's law* – see among others [12–18].

Other Authors describe migration via Equation (2), e.g. Refs. [19–21]. In all the aforementioned models, the electric field is not constrained in any way to satisfy Maxwell's equations. Remarkably, paradoxically as stated in Ref. [22], it does violate¹ Maxwell's equations (see for instance [19], Fig. 3 and comments therein).

Equation (2) reflects physical properties of the processes in an average sense and has to be considered as an approximation, as pointed out in Ref. [22]. An excellent discussion on the origin of Equation (2) can also be found there in terms of the ratio²

$$r_D = \sqrt{\frac{1}{2} \frac{\epsilon}{c_{\text{bulk}}} \frac{RT}{F^2}} \quad (3)$$

termed Debye length. It assesses a charge electrostatic effect in the electrolyte solution, and measures how far those effects persist. The Debye length is typically in the order of nanometers or even below in battery cells electrolyte (see Section 7).

In multi scale approaches [3], the electroneutrality assumption (2) cannot be used as in Newman's theory, since it does not allow to perform correct scales transitions. This is of major importance for researchers who want to understand and optimize the battery behavior with multi-scale models. In fact, in the rigorous mathematical formulation of multi scale modeling – see Refs. [23,24] – the micro to macro scale transition requires conservation of power expenditure between both scales, thus assuring that energy is neither artificially generated nor artificially dissipated across the scales. If electro-neutrality is used in place of Maxwell's equations, recovering the energy description of the electromagnetic interactions is not possible.

For this sake, in Ref. [3] and in the present paper, Equation (2) is not used as a fundamental law. Instead, the electro-magnetics is explicitly taken into account via the *electro-quasi-static* formulation [25] of Maxwell's equations, which is summarized in Section 2. Inductive effects are not included, yet the effect of the magnetizing field is taken into account by means of Maxwell's correction within Ampère's law. This is major novelty of the proposed approach, in which electroneutrality is an outcome of the problem solution. The numerical simulations performed in Section 7, where real battery data are considered, reveal that the deviation from electroneutrality is as small as expected, ten orders of magnitude with respect to the equilibrium electrolyte concentration, in agreement with the literature (see Refs. [1], page 286 and [26]).

Electroneutrality can be used to identify the relevance of external actions, in order to simplify the model. For the balance of momentum, Lorentz's forces are indeed related to the deviation from electroneutrality. The effect of such forces appears to be of second order compared to the effects of surface tractions of mechanical origin.

The following basic hypotheses will also be assumed: i) the paper does not focus on the double layer in which electrochemical reactions occur; ii) in the absence of *convection*, movement of species is governed by *diffusion*, driven by gradients of concentration, and by *migration* driven by the electric field; iii) displacements and strains are *small*; iv) the binary electrolyte is a solution of a binary salt (say LiX , where X can for instance be PF_6 , consisting of only two molecules in which both are ions, a cation (Li^+) and an

¹ This is immediately accomplished in 1D, where in view of electroneutrality Gauss law reads $\frac{\partial D}{\partial x} = 0$, thus leading to a constant electric field.

² ϵ [$\text{A}^2 \text{s}^2 \text{N}^{-2} \text{m}^{-2}$] stands for the permittivity of the medium in which ionic transport takes place, c_{bulk} [mol m^{-3}] for the bulk concentration of salt LiX , T [K] for the temperature, R [$\text{J K}^{-1} \text{mol}^{-1}$] for the universal gas constant, F [As mol^{-1}] for Faraday's constant. The Debye length r_D is therefore measured in Ref. m.

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