

PhD position – Multiscale modeling of the porous electrodes of lithium-ion batteries based on reconstructed 3D microstructures

Important information

We are looking for someone with a strong background in physics, mechanics or applied mathematics. Knowledge on transport in porous media and upscaling methods, such as homogenization or volume averaging, would also be greatly appreciated.

- DATES: Three-year PhD position, starting date between June and October 2022.
- LOCATION: Institut de Mécanique des Fluides de Toulouse (IMFT), Toulouse, France.
- SALARY: About 32k euros gross / year.
- SUPERVISORS: IMFT (Yohan Davit, Olivier Liot), CIRIMAT (Céline Merlet), TotalEnergies (Romain de Loubens)

Context and scientific project

Lithium-ion batteries (LIB) are the primary energy storage technology for modern portable electronic devices such as laptop computers, tablets and mobile phones. They can also provide stationary storage for renewable energies, and are at the core of the transition towards electric vehicles. LIBs are foreseen to remain the dominant technology for the foreseeable future, with an enormous increase in demand. Improving the performance and safety of LIBs is therefore an important research area. Besides its role in understanding fundamental mechanisms, modeling of LIBs is key in defining robust state observers that can be used for safe control in the battery management system. Modeling is also helpful in assessing ageing or in optimizing the operating conditions and the battery cell design. The so-called “Porous Electrode Theory” introduced in the 1970’s is the current state of the art in modeling LIBs at cell level. It consists in a mixed formulation, where transport equations are averaged for the electrolyte phase and the exchange flux between phases is modeled by locally solving the microscale transport equation in the active material (solid).

Our goal is to develop new models of LIBs that can exploit advances in sub-micron scale imaging and high-performance computing (HPC). To do so, we will work on direct upscaling of transport equations in the different LIB components (Figure 1), the positive electrode, the separator and the negative electrode. The idea is to obtain average formulations involving effective parameters that can be directly calculated through resolution of closure problems over representative geometries based upon real images of battery structures. The project will start with both a postdoctoral position and a PhD studentship. The postdoctoral researcher will focus on upscaling for the separator, whereas the PhD student will first focus on the negative electrode. In the negative electrode, the active material for lithium (de)-insertion consists of natural or synthetic graphite, with a mean particle size around 5 micrometers. The electrode also contains a small fraction of polymer binder which is needed to improve mechanical

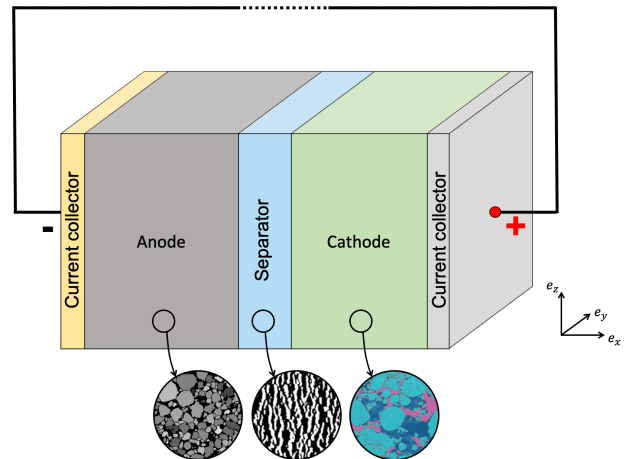


Fig. 1: Schematic view of a LIB cell

stability. Finally, the available pore space between graphite particles, representing a volume fraction of about 30%, is filled by a liquid electrolyte that is highly concentrated in lithium salt (e.g., LiPF₆).

To illustrate the mathematical formulation of the microscale transport problem, a simplified set of equations is presented below. Let T be a timescale of interest and $\Omega = \Omega_s \cup \Omega_e$ denote the electrode domain, consisting of a solid phase Ω_s and a liquid (electrolyte) phase Ω_e . The microscale equations for mass and charge transport in $\Omega_s \times [0, T]$ are given by

$$\frac{\partial c_s}{\partial t} = -\nabla \cdot \mathbf{N}_s = \nabla \cdot (D_s \nabla c_s), \quad (1)$$

$$0 = -\nabla \cdot \mathbf{i}_s = \nabla \cdot (\sigma_s \nabla \phi_s), \quad (2)$$

where c_s , ϕ_s , D_s and σ_s denote the intercalated lithium concentration, the electric potential, the lithium diffusion coefficient and the electronic conductivity, respectively. In $\Omega_e \times [0, T]$, electrolyte concentration c_e and ionic potential φ_e satisfy the following conservation equations

$$\frac{\partial c_e}{\partial t} = -\nabla \cdot \mathbf{N}_e = \nabla \cdot \left(D_e \nabla c_e - \frac{t_+^0}{F} \mathbf{i}_e \right), \quad (3)$$

$$0 = -\nabla \cdot \mathbf{i}_e = \nabla \cdot \left(\kappa_e \nabla \varphi_e - \frac{2RT(1-t_+^0)}{F} \kappa_e \nabla \ln c_e \right). \quad (4)$$

The right-hand side of Eq. 3 contains the contributions of diffusion and electric migration to the total ionic flux, \mathbf{N}_e . D_e is an inter-diffusion coefficient, t_+^0 the Li⁺ transference number, and F is Faraday's constant. The divergence-free current density \mathbf{i}_e satisfies a modified Ohm's law where κ_e is the ionic conductivity. At the interface $\Gamma_{se} = \bar{\Omega}_s \cap \bar{\Omega}_e$, the charge-transfer reaction kinetics are classically modeled by the Butler-Volmer equation,

$$i_{se} = Fk_0 c_s^{1-\alpha} c_e^\alpha (c_{s,\max} - c_s)^\alpha \left(e^{\frac{\alpha F}{RT} \eta} - e^{-\frac{(1-\alpha)F}{RT} \eta} \right), \quad \eta = \phi_s - \varphi_e - U_0(c_s), \quad (5)$$

with the following interface conditions,

$$\mathbf{i}_s \cdot \mathbf{n} = \mathbf{i}_e \cdot \mathbf{n} = F\mathbf{N}_s \cdot \mathbf{n} = F\mathbf{N}_e \cdot \mathbf{n} = i_{se}, \quad (6)$$

where \mathbf{n} is the interface normal pointing toward the electrolyte. In Eq. 5, i_{se} is the interface current density, k_0 the reaction rate constant, α the anodic strength coefficient, $c_{s,\max}$ the maximum intercalated Li concentration, and U_0 the equilibrium potential of the electrode's active material vs. lithium metal.

The PhD student will

1. use upscaling methods to derive average transport for the coupled, non-linear system of mass and charge conservation equations (Eqs. 1 to 6, or a more complex version accounting for composite electrode structures and/or additional physics)
2. use HPC direct numerical simulations (DNS) of mass and charge conservation at pore-scale to aid in determining adequate hypotheses for upscaling. TotalEnergies is developing a code for this purpose and will provide support to train and assist the PhD student.
3. compare the results of the average formulation with that of DNS in simple model geometries.
4. calculate effective parameters for real electrode geometries. The images will be provided by Saft and TotalEnergies. The code for solving the closure problem will be developed in collaboration with TotalEnergies.

Contacts

If you are interested, please send a resume to the following addresses and use "PhD_LIB_application" as the title of your e-mail.

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