Abstract

Lithium-ion batteries (LIBs) are the backbone of today's portable electronics, electric mobility and grid integration thanks to intercalation chemistries supplanting metallic-lithium anodes. However, accelerating innovation is hampered by costly, material-intensive experimentation and by models that either oversimplify electrode morphology or are too slow for decision-making. This thesis addresses both challenges by (i) building a high-fidelity, pore-scale 4D model (3D in space + time) that resolves morphology-induced heterogeneity of concentration and potential; and (ii) deriving a fast, physics-based surrogate via rigorous homogenization to predict charge–discharge behavior with quantified accuracy. The most employed computational model for charge-discharge simulation of LIBs is the so called pseudo-2D Doyle–Fuller–Newman (P2D/DFN) framework, which assumes monodisperse spherical particles and lateral uniformity. While effective for long cycling, this approximation is inadequate for graphite anodes: their flake-like, anisotropic microstructure alters transport pathways, reaction surface availability, and local overpotentials. To capture these effects, we developed an automated workflow that automatically generates pore-scale COMSOL Multiphysics models through the Java API. All geometric and physicochemical inputs, such as particle positions, size distributions, anisotropic diffusion, kinetics and electrolyte properties, are supplied via human- and machine-readable text files, enabling rapid, reproducible campaign design and large-scale dataset creation. We employed this script to construct three anode morphologies of increasing realism: monodisperse spheres, polydisperse spheres, and polydisperse triaxial ellipsoids. This last kind of geometrical representation was selected to approximate the flat morphology of graphite while preserving credible inter-particle contacts. Transient simulations resolved the coupled mass and charge transport in solid and liquid phases with Butler-Volmer boundary condition enforced on the solid–electrolyte interfaces. We quantified intra-particle lithiation patterns, pore-scale concentration gradients, and the resulting voltage response. Discharge curves

and morphological quantities were compared with experimental data, demonstrating that the three system generated were similar enough to be compared. We concluded that ellipsoidal ensembles reproduce spatial heterogeneity and effective kinetics more faithfully than sphere-based models, highlighting the sensitivity of performance to porosity and particle size dispersion. Second, to enable near-real-time inference without sacrificing morphological insight, we searched for a an accurate model, that can deliver the requested response in few seconds. Therefore we decided to adopt homogenization via multiple-scale asymptotic expansion to derive macroscopic equations for coupling diffusion–electromigration–reaction with a rigorous mathematical framework. Under standard LIB scale separation (pore size ℓ « electrode thickness L) and periodicity assumptions, we obtained closed-form cell-scale balances augmented by morphology-dependent effective transport tensors. Boundary conditions at the current collectors were included explicitly, obtaining a mathematical relationship that links micro-scale geometry, represented by the geometrical scale parameter $\varepsilon = \ell/L$, to macro-scale operating conditions, expressed by the external applied electric current density. The upscaled model has been verified against pore-scale simulations for concentration and voltage, and we mapped applicability regimes and error estimation in terms of the geometrical scale parameter ε. Within these regimes the reduced-order predictive model well reproduces full-order dynamics at a fraction of the cost, with a designable control over the error, supporting in-line estimation tasks such as state-of-health tracking where latencies of seconds are required.