Engineering Frameworks for Reaction-Limited Porous Electrodes

by

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ABSTRACT

Lithium-ion batteries are central to the global transition toward electrified transportation and grid-scale renewable energy storage. Predictive models that span the full range of relevant electrochemical phenomena from interfacial charge transfer to electrode-scale transport and mechanical deformation are essential for advancing battery design, diagnostics, and lifetime management. However, existing high-fidelity models are constrained by scarce real-world data and compute-time constraints, while empirical or black-box reduced-order models sacrifice physical interpretability and accuracy. This thesis develops a suite of engineering frameworks for porous electrodes, with a unifying emphasis on coupled ion–electron transfer (CIET) kinetics, non-equilibrium thermodynamics, interpretability, and computational efficiency suitable for real-world battery innovation and management.

The first contribution establishes the experimental and theoretical case for CIET as the appropriate kinetics framework for Li-ion intercalation. Comprehensive kinetic measurements across multiple electrode and electrolyte chemistries reveal a universal dependence of the exchange-current density on the Li-ion vacancy fraction, consistent with a concerted ion–electron transfer mechanism. The CIET model collapses all data onto master curves as functions of overpotential and filling fraction, providing a physically grounded alternative to the phenomenological Butler–Volmer equation. The newly discovered overpotential and filling fraction dependencies form a basis for quantifying charge transfer in predictive models developed in this thesis.

The second contribution develops a scaling analysis and lean-model approximation of porous electrode theory (PET) for reaction-limited solid-solution electrodes. Closed-form solutions for galvanostatic voltage curves, impedance spectra, and chronoamperometric responses are organized by four physically transparent dimensionless groups associated with process rate, wiring, electrolyte transport, and capacitive charging, and are validated against full numerical simulations, achieving quantitative agreement under practical operating conditions while reducing computational cost by orders of magnitude.

The third contribution extends this framework to phase-transforming electrodes through a coarse-grained population balance model. A description of particle population fractions and corresponding zones is coupled to zone-wise analytical overpotential solutions and cast as an equivalent circuit, capturing the essential physics of voltage plateaus and hysteresis in multiphase porous electrode theory at a fraction of the computational cost.

The fourth contribution develops a network-based fractional derivative model that treats the electrode as a graph of particles coupled by electronic conductances. For particle networks with broad power-law contact conductance distributions, the macroscopic admittance takes a fractional-order form, providing a particle network-based mechanistic derivation of the ubiquitous constant-phase element in electrochemical impedance spectra. The fractional model is further motivated by a Fractional Relaxation Impedance (FRI) method that independently supports CIET kinetics in lithium cobalt oxide cathodes.

The fifth contribution presents a millisecond-scale electro-chemo-mechanical model for cycling-induced electrode deformation. Drucker–Prager/Cap powder plasticity is implemented within PET, capturing both reversible and irreversible thickness changes validated against experimental cycling data.

Together, these frameworks push the frontier of physics-based high-fidelity battery modeling that is computationally efficient. By bridging microscale physics with macroscopic observables, this work provides a foundation for physics-guided battery design, parameter identification, and degradation analysis in next-generation energy storage systems.

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