

Multiscale Modelling of Ionic Conduction in Advanced Battery Materials

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ABSTRACT

The rigorous simulation of electrical conduction in rechargeable batteries is a complex task spanning several orders of magnitude in both time and length scales. Electronic phenomena such as polarizability, occurring at the sub-angstrom level over tens of attoseconds, can significantly impact the diffusion of charge-carriers across tens of nanometers during hundreds of nanoseconds. If the electrode or electrolyte material displays phase separation, the transport of charge-carriers will depend on the diffusivity within the individual phases (~ 10 nm) and the manner in which the phases are mixed (~ 100 nm). Interfacial contacts such as grain boundaries or the boundary between polymeric and crystalline regions in mixed-matrix solid electrolytes can increase the relevant time-scales up to microseconds, due to slow diffusion. Consequently, different modelling strategies must be integrated in order to yield physically meaningful predictions. In this work, we present two examples in which ionic transport in Li- and Na-ion battery materials is described by combining several spatiotemporal scales in a consistent fashion [1, 2]. First, we show how structural data extracted from density functional theory calculations can be employed for the development of a polarizable force field capturing the interatomic forces in NaFePO₄, a promising cathode for Na-ion batteries [3]. By combining this force field with accurate atomistic sampling techniques, the mechanisms underlying the transport of Na-ions at different Na concentrations are revealed with unprecedented detail. In particular, we employ an in-house enhanced atomistic sampling scheme based on hybrid Monte Carlo (HMC) called the Randomized Shell Mass - Generalized Shadow HMC (RSM-GSHMC) [4], which we further strengthen with multi-stage adaptive integrators recently developed in our group [5]. In the following example, we combine atomistic simulations and Bruggeman's effective medium approximation to describe the diffusion of Li-ions in Al-substituted Li₇La₃Zr₂O₁₂ (LLZO), the most relevant solid electrolyte material to date for Li-ion batteries [6]. Experiments have shown that at low concentrations of Al, LLZO can exist simultaneously in two phases: a highly conductive cubic phase and a poorly conductive tetragonal phase. We use GSHMC and Molecular Dynamics (MD) simulations to obtain the diffusivity within each phase. Subsequently, we employ Bruggeman's model (which operates at a length scale much larger than that of individual Li-ion jumps) to extract the diffusivity of the multi-phase material.

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