

A MODEL PROBLEM CONCERNING THE IONIC TRANSPORT IN MICROSTRUCTURED SOLID ELECTROLYTES

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Abstract. Current efforts to develop polymeric electrolytes for all-solid-state lithium batteries are hampered by the unsatisfactory ionic conductivity of available polymers at room temperature. The most promising polymers available to date consist of poly-ethylene-oxide (PEO) complexes doped with a lithium salt such as lithium perchlorate (LiClO_4) or lithium iodide (LiI). These are semi-crystalline polymers which often exhibit spherulitic microstructural morphologies. Now, early experimental works on semi-crystalline polymers claimed that only the amorphous phase supported fast ionic transport, thus promoting efforts to produce PEO complexes of low crystallinity. However, more recent works have revealed that when a PEO specimen is deformed the ionic conductivity in the direction of elongation increases by orders of magnitude. This strongly suggests that actually the crystalline phase can be more conductive than the amorphous phase in certain directions, and that highly conductive PEO complexes could result from high crystallinities with suitable crystallographic textures. The purpose of this work is to develop a multi-scale constitutive theory that rationalize these observations.

We begin by deriving the field equations of ionic transport in microstructured solids by combining the principles of mass conservation, electrodynamics, and thermodynamics in a consistent fashion. We consider common forms of the energies and dissipation rates characterizing the various phases. The nonlinear field equations are then homogenized by making use of the notion of two-scale convergence. At the microscopic scale, the various field equations become a set of decoupled linear conductivity equations; at the macroscopic scale, the field equations remain nonlinear but the effective behavior is characterized by a set of second-order conductivity tensors which can be computed by traditional means. The theory is applied to two-dimensional material systems with spherulitic microstructural morphologies. These microstructures are modeled with two-scale microgeometries consisting of Shulgasser's spheres (higher length scale) composed of two-phase laminates (lower length scale) radially oriented. An analytic expression is obtained for the ionic conductivity in terms of the various microstructural parameters, including the crystallinity. Assuming reasonable values for the various material parameters characterizing the amorphous and crystalline phases, the predictions do support the idea that the crystalline phase exhibits a higher (lower) ionic mobility than the amorphous phase along (perpendicular to) the direction of the polymeric chains.