

A model problem concerning the ionic transport in microstructured solid electrolytes

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Abstract

We consider ionic transport by diffusion and migration through microstructured solid electrolytes. The effective response is determined by homogenizing the relevant field equations via the notion of multi-scale convergence. The theory is applied to semi-crystalline polymer electrolytes with spherulitic morphologies. Predictions support recent experimental observations on doped poly-ethylene-oxide (PEO) systems which suggest that the anisotropic crystalline phase can actually support faster ion transport than the amorphous phase along certain directions dictated by the morphology of the polymeric chains.

Keywords: Diffusion, migration, heterogeneous solids, periodic homogenization

1 Motivation

Solid-state batteries present numerous advantages over conventional liquid or gel-electrolytes batteries in terms of safety, design simplicity, durability, and mechanical flexibility. These capabilities offer the potential of packing batteries inside mechanical structures to constitute so called ‘structural batteries’, which could lead to significant gains in weight and space. This is of particular importance in micro- and nano-satellites, where the batteries and supporting structures can represent up to 25% of the total mass.

However, 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 polymer electrolytes 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 often exhibiting spherulitic microstructures. Early studies on different polymer complexes revealed that a transition from highly activated to easy ion transport with varying temperature was always accompanied by a considerable reduction in crystallinity (Berthier et al., 1983). This observation led to the widespread belief that only the amorphous phase could support fast ion transport in semi-crystalline polymers. Since then, efforts have focused on producing polymer complexes with minimal crystallinity levels. However, more recent studies have revealed that the ionic conductivity of PEO complexes can increase by several orders of magnitude when specimens are subjected to large stretchings (e.g., Minami et al., 2005). This observation strongly suggests that the anisotropic crystalline phase can actually support faster ion transport than the amorphous phase along certain directions that become aligned with the principal axes of deformation. In fact, crystalline PEO is known to consist of monoclinic unit cells of aligned chains exhibiting a helical configuration which may permit fast ion transport along the helical axis. This suggests, in turn, that highly conductive

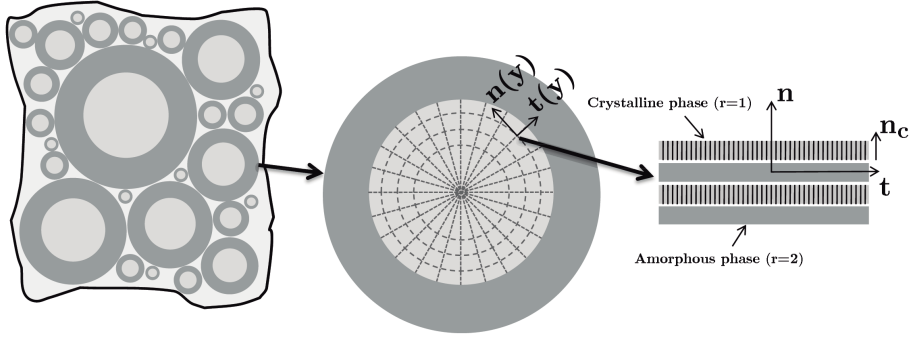


Figure 1: Schematic of the Schulgasser's sphere assemblages utilized in the model.

PEO complexes could be obtained by tuning the crystallographic texture rather than reducing the crystallinity. This work provides multi-scale theoretical predictions that support this conjecture.

2 A multi-scale model for semi-crystalline polymer electrolytes

2.1 Assumptions and formulae

The focus here is on semi-crystalline polymer electrolytes exhibiting spherulitic microstructures. For definiteness, we take the PEO systems doped with LiClO_4 of Fullerton-Shirey & Maranas (2009) as a case study. In these systems the PEO molecules dissolve the LiClO_4 salt into Li^+ and ClO_4^- univalent ions ($z_\alpha = 1$) and form various phases depending on salt concentration and temperature. At room temperature, their microstructural morphology is a two-scale structure formed by alternating layers of crystalline and amorphous phases in intimate contact with each other at the lower nanometer scale, which in turn radiate out from various center points in the specimen, leading to morphological structures at the larger micrometer scale known as spherulites. Depending on salt concentration, the spherulites can either form a granular aggregate or be separated by a continuous amorphous matrix, and the volume fraction of the crystalline phase can range from 10% to 90%. At the molecular scale, the crystalline phase consists of monoclinic unit cells of aligned polymer chains exhibiting a helical configuration.

We derive a multi-scale model for these material systems by constructing (two-dimensional) microgeometries which, on the one hand, are complex enough to reproduce the essential geometrical features of the above microstructures, but on the other hand, are simple enough so that their homogenized response can be computed exactly via the notion of multi-scale convergence of Allaire & Briane (1996). The microgeometries of choice consist of a combination of a Schulgasser's cylinder assemblage and simple laminates. At the mesoscale, these microgeometries are assemblages of homothetic cylinders of infinite sizes filling up the entire unit cell, each composed of an isotropic exterior coating of amorphous phase and a radially symmetric interior core or cylindrulite. At the microscale, the cylindrulite is in turn a laminated microgeometry composed of alternating laminae of amorphous and crystalline phases with the lamination direction coincident with the mesoscale tangential direction. A schematic of the microgeometries is shown in figure 1.

The microstructural parameters of the model are the volume fractions of the cylinders occupied by the amorphous rings f_r and by the cylindrulites f_c , and the volume fractions of the lamellar structure within the cylindrulite occupied by the amorphous phase f_c^a and by the crystalline phase f_c^{cr} . These parameters satisfy the identities

$$f_r + f_c = 1, \quad \text{and} \quad f_c^a + f_c^{cr} = 1. \quad (1)$$

The total volume fractions of crystalline and amorphous phases are thus given by

$$f^{(cr)} = f_c f_c^{cr} \quad \text{and} \quad f^{(a)} = f_c f_c^a + f_r, \quad (2)$$

respectively, and are such that $f^{(cr)} + f^{(a)} = 1$; the volume fraction $f \equiv f^{(cr)}$ represents the crystallinity of the electrolyte.

Within phase r of the microstructured electrolyte, the electrochemical potential μ_α and the flux \mathbf{j}_α of ionic species α are assumed to depend on the electric potential ϕ and molar concentration c_α as

$$\mu_\alpha = RT \ln \frac{c_\alpha}{c_{0\alpha}^{(r)}} + F z_\alpha \phi \quad \text{and} \quad \mathbf{j}_\alpha = -c_\alpha \mathbf{M}_\alpha^{(r)} \nabla \mu_\alpha, \quad (3)$$

where F is Faraday's constant, RT is the universal gas constant times the temperature, $c_{0\alpha}^{(r)}$ is a reference molar concentration, and $\mathbf{M}_\alpha^{(r)}$ is a mobility tensor. The mobility tensors of both ion types in the isotropic amorphous phase and the anisotropic crystalline phase are taken to be, respectively,

$$\mathbf{M}_\alpha^{(a)} = m_\alpha^a \mathbf{I} \quad \text{and} \quad \mathbf{M}_\alpha^{(cr)} = m_\alpha^\parallel \mathbf{n}_c \otimes \mathbf{n}_c + m_\alpha^\perp (\mathbf{I} - \mathbf{n}_c \otimes \mathbf{n}_c), \quad (4)$$

where m_α^\parallel and m_α^\perp represent mobilities along the directions parallel and perpendicular to the direction \mathbf{n}_c of the chain axes.

The corresponding weighted mobility tensors \mathbb{M}_α are given by

$$\mathbb{M}_\alpha^{(a)} = \eta_\alpha^{(a)} \mathbf{I} \quad \text{and} \quad \mathbb{M}_\alpha^{(cr)} = \eta_\alpha^\parallel \mathbf{n}_c \otimes \mathbf{n}_c + \eta_\alpha^\perp (\mathbf{I} - \mathbf{n}_c \otimes \mathbf{n}_c), \quad (5)$$

with

$$\eta_\alpha^{(a)} = \frac{c_{0\alpha}^{(a)}}{f^{(cr)} c_{0\alpha}^{(cr)} + f^{(a)} c_{0\alpha}^{(a)}} m_\alpha^{(a)} \quad \text{and} \quad \eta_\alpha^{\parallel,\perp} = \frac{c_{0\alpha}^{(cr)}}{f^{(cr)} c_{0\alpha}^{(cr)} + f^{(a)} c_{0\alpha}^{(a)}} m_\alpha^{\parallel,\perp}. \quad (6)$$

Here, $c_{0\alpha}^{(cr)}$ and $c_{0\alpha}^{(a)}$ are the reference concentrations of the crystalline and amorphous phases, respectively. The overall response is obtained sequentially by first homogenizing the laminated structure to obtain the mesoscopic mobilities, and then homogenizing Schulgasser's assemblage to obtain the macroscopic mobilities. The ensuing analysis is greatly simplified by assuming that the chain axes \mathbf{n}_c are aligned with the lamination direction \mathbf{n} . This amounts to disregarding chain tilting. Thus, the axes of anisotropy of the mesoscopic mobility tensors are radially aligned within the cylindrites. Granted this assumption, the effective mobilities in the lamellae structure can be written as —see, for instance, Milton (2002)—

$$\tilde{\mathbb{M}}_\alpha(\mathbf{y}) = \tilde{\eta}_\alpha^\parallel \mathbf{n}(\mathbf{y}) \otimes \mathbf{n}(\mathbf{y}) + \tilde{\eta}_\alpha^\perp [\mathbf{I} - \mathbf{n}(\mathbf{y}) \otimes \mathbf{n}(\mathbf{y})], \quad (7)$$

where $\mathbf{n}(\mathbf{y})$ is lamination direction at position \mathbf{y} in the Schulgasser assemblage, and the parallel and perpendicular mesoscopic effective mobilities are given by

$$\tilde{\eta}_\alpha^\parallel = \left(\frac{f_c^{cr}}{\eta_\alpha^\parallel} + \frac{f_c^a}{\eta_\alpha^{(a)}} \right)^{-1} \quad \text{and} \quad \tilde{\eta}_\alpha^\perp = f_c^{cr} \eta_\alpha^\perp + f_c^a \eta_\alpha^{(a)}. \quad (8)$$

Thus, the axes of anisotropy of the mesoscopic mobility tensors are radially aligned within the cylindrites. This allows the use of Schulgasser's solution scheme to obtain the macroscopic mobility tensors $\overline{\mathbb{M}}_\alpha$, which yields

$$\overline{\mathbb{M}}_\alpha = \overline{\eta}_\alpha \mathbf{I} \quad (9)$$

with

$$\bar{\eta}_\alpha = \eta_\alpha^{(a)} \frac{(1 - f_c)\eta_\alpha^{(a)} + (1 + f_c)\sqrt{\tilde{\eta}_\alpha^\parallel \tilde{\eta}_\alpha^\perp}}{(1 + f_c)\eta_\alpha^{(a)} + (1 - f_c)\sqrt{\tilde{\eta}_\alpha^\parallel \tilde{\eta}_\alpha^\perp}}. \quad (10)$$

Expression (10), together with (6) and (8), constitute a closed-form estimate for the mobilities of each ion species through the model semi-crystalline polymer in terms of the local mobilities of the amorphous and crystalline phases, and the various microstructural parameters. Details of the derivation of this expression are given in Curto Sillamoni & Idiart (2014).

2.2 Results and discussion

Here we present a selected set of numerical results to explore the dependence of the macroscopic mobilities on the various material and microstructural parameters. We begin by considering

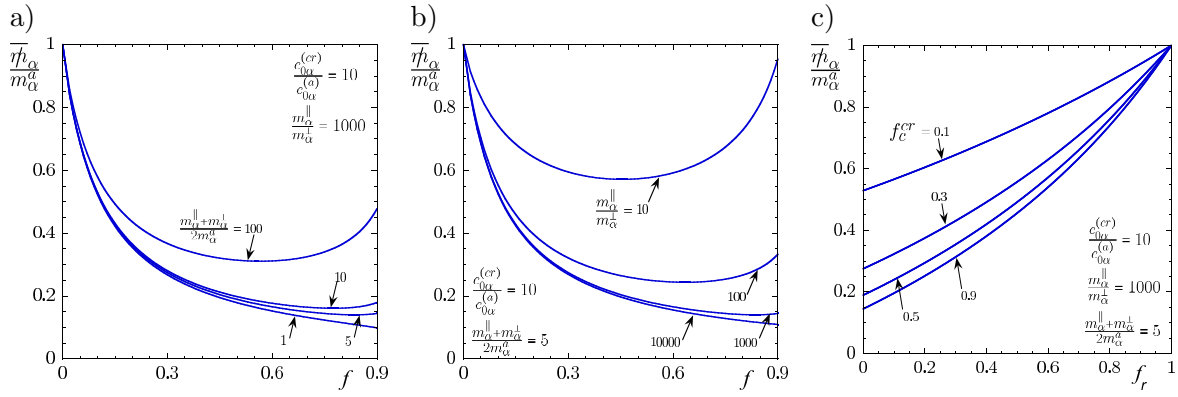


Figure 2: Effective mobility of species α in a semi-crystalline polymer electrolyte. Plots a) and b) without amorphous rings ($f_c = 1$) versus crystallinity f . Plots for: (a) $c_{0\alpha}^{(cr)}/c_{0\alpha}^{(a)} = 10$, $m_\alpha^\parallel/m_\alpha^\perp = 1000$, and various mobility contrasts $(m_\alpha^\parallel + m_\alpha^\perp)/(2m_\alpha^a)$; (b) $c_{0\alpha}^{(cr)}/c_{0\alpha}^{(a)} = 10$, $(m_\alpha^\parallel + m_\alpha^\perp)/(2m_\alpha^a) = 5$, and various mobility anisotropy ratios $m_\alpha^\parallel/m_\alpha^\perp$; (c) case with amorphous ring, plotted versus ring volumetric fraction f_r , with $(m_\alpha^\parallel + m_\alpha^\perp)/(2m_\alpha^a) = 5$, $m_\alpha^\parallel/m_\alpha^\perp = 1000$, $c_{0\alpha}^{(cr)}/c_{0\alpha}^{(a)} = 10$, and various cylindrilite crystallinity fraction f_c^{cr} . The results are normalized by the corresponding mobility m_α^a in the amorphous phase.

material systems with no amorphous ring ($f_c = 1$). The results are parameterized by the reference concentration contrast $c_{0\alpha}^{(cr)}/c_{0\alpha}^{(a)}$, the mobility contrast $(m_\alpha^\parallel + m_\alpha^\perp)/(2m_\alpha^a)$, and the mobility anisotropy ratio of the crystalline phase $m_\alpha^\parallel/m_\alpha^\perp$. We assume that the mobilities are such that $m_\alpha^\perp \leq m_\alpha^a \leq m_\alpha^\parallel$. Moreover, given that the ratio of PEO ether oxygens to lithium ions in the crystalline phase is typically lower than in the amorphous phase, we assume that $c_{0\alpha}^{(cr)}/c_{0\alpha}^{(a)} \geq 1$. Figure 2 shows predictions for the effective mobility \bar{m}_α of species α , normalized by the corresponding mobility in the amorphous phase m_α^a , as a function of crystallinity f , for a wide range of material parameters. It is recalled that these results are the same for both ionic species α . The main observation in the context of this figure is that the effective mobility can decrease with increasing crystallinity even when the mobility in the crystalline phase along the chain axis is orders of magnitude higher than the mobility of the amorphous phase. In fact, the predictions provided in parts (a) and (b) show that for sufficiently low mobility contrasts (≤ 5) and large mobility anisotropy ratios (≥ 1000) the effective mobility decreases monotonically with crystallinity, by up to an order of magnitude, in the range $0 \leq f \leq 0.9$. This shows that the decrease in ionic conductivity with crystallinity commonly observed in semi-crystalline polymer electrolytes *does not imply* a faster ionic transport in the amorphous phase than in the crystalline phase, as originally proposed by Berthier et al. (1983). Moreover, while this model does not account for the effect of mechanical deformations, it is clear that the above predictions provide

a plausible mechanistic explanation for the increase in ionic conductivity observed in stretched electrolytes (Golodnitsky & Peled 2000; Golodnitsky et al., 2001; Minami et al., 2005). Indeed, upon stretching a material system with the above characteristics, the polymer chains in both the amorphous and crystalline phases tend to align with the stretching direction (Burba et al., 2011); the effective mobility along the stretching direction should thus tend to m_{α}^{\parallel} . For the choice $c_{0\alpha}^{(cr)}/c_{0\alpha}^{(a)} = 10$, $m_{\alpha}^{\parallel}/m_{\alpha}^{\perp} = 1000$ and $(m_{\alpha}^{\parallel} + m_{\alpha}^{\perp})/(2m_{\alpha}^{(a)}) = 5$, the mobility m_{α}^{\parallel} can be two orders of magnitude larger than the predicted effective mobility for (unstretched) systems with moderate crystallinity levels. This is approximately the increase reported by Gitelman et al. (2008) in PEO systems doped with LiI.

Finally, part (c) shows the effect of the amorphous ring ($f_r > 0$) on the effective mobility for various choices of cylindrulte crystallinity (f_c^{cr}). The mobility is seen to increase monotonically with f_c^{cr} , as expected. As already mentioned, the size of the amorphous rings in real material systems increases with salt concentration (Fullerton-Shirey & Maranas, 2009). The presence of amorphous rings can thus introduce non-monotonic trends in the predictions for the effective conductivity as a function of salt concentration. Such dependence remains to be explored and will be reported in due time.

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