Molecular simulation of the solid-state transport properties of silver sulfide towards smart passivation strategies for silver nanowires in the environment

P. SIMONNIN [1], L. CHARLET [2], B. GILBERT [3], K. ROSSO [4]

[1] ISTerre 1381 rue de la Piscine, 38610 Gières, FRANCE, simonnin.pauline@gmail.com
[2] ISTerre 1381 rue de la Piscine, 38610 Gières, FRANCE, charlet38@gmail.com
[3] Berkley Lab, 1 Cyclotron Rd, Berkeley, CA 94720, USA, bgilbert@lbl.gov
[4] PNNL, 902 Battelle Blvd, Richland, WA 99354, USA, kevin.rosso@pnnl.gov

The high electric conductivity, low cost and optical properties of silver nanomaterials, especially nanowires, has led to their rapid emergence in the manufacture of new electronic devices, such as touch screen technology and photovoltaics. However, because of the potential for Ag^+ release and the higher risk of cellular penetration due to the wire shape,their cytotoxicity has raised health concerns for humans and other organisms. In that context, developing a safer-by-design strategy for silver nanowires is a key factor in manufacturing and commercializing safe and effective nanomaterial enabled devices. Sulfidation of the surface to Ag_2S is an important natural passivation process but with poorly understood structure and consequences on nanowire redox reactivity and cytotoxicity. Here we report ab initio molecular dynamics simulations directed at understanding the mechanisms of electrical conduction in Ag_2S polymorphs of acanthite and argentite, which in bulk are related by a phase boundary at 450 K. The simulations accurately recover these respective structures, and reveal the superionic conduction nature of the higher temperature phase argentite. A structural analysis between the low (300 K) and high (450 - 600 K) temperature phases suggest very minor structural modifications, making the phase transition barely perceptible. For the high temperature phase, we found that silver atoms diffuse in a liquid-like behavior in three dimensions within a relatively rigid close-packed sulfur sublattice, with predicted diffusivities that match well with experimentally measured value. Ongoing work will examine the effects of progressively reduced dimensionality on the conduction properties of these two polymorphs towards thin film geometries consistent with passivation layers on silver nanowire surfaces.