On the Ambiguous Influence of Soft Lattices on Ionic Transport

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The advent of solid-state batteries has sparked a rise in the interest in lithium conducting solid electrolytes, especially lithium thiophosphates.[1] These materials are intrinsically soft in nature, which has always been believed to be beneficial for ionic transport. It is generally assumed that ion transport comes with lower activation barriers in softer, more polarizable lattices.[2] Within a highly polarizable lattice, the anions can be displaced more easily and the energetic cost for moving an ion is much smaller. This chemical intuition has been corroborated by the existence of good conduction in materials possessing iodine or sulfide anions, relative to the stiffer and less polarizable oxides.

Here, we demonstrate direct experimental correlations between lattice softness and ionic transport in a Li^+ conducting material using various structural and transport measurement techniques (e.g. X-ray diffraction and electrochemical impedance spectroscopy, respectively). A series of solid solutions with tunable lattice polarizability will be presented in which no changes to the diffusion pathways can be observed, yet significant changes in the ionic transport occur due to a softening of the lattice. With decreasing bond-strength (i.e. increasing polarizability), the activation barriers indeed decrease as expected. However, the increasing softness of the lattice detrimentally affects the Arrhenius pre-factor preventing a higher conductivity with increasing lattice polarizability. These data show that the current belief of, "the softer, the better" needs to be revisited.

References:

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[2] J. C. Bachman, S. Muy, A. Grimaud, H.-H. Chang, N. Pour, S. F. Lux, O. Paschos, F. Maglia, S. Lupart, P. Lamp, Chem. Rev. 182 (2015) 53–58.