Millisecond Ion-Transport Simulations of Mixed Polyanion Solid Electrolytes

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Lithium and sodium (Na) mixed polyanion solid electrolytes for all-solid-state batteries display some of the highest ionic conductivities reported to date. However, the effect of polyanion mixing on ion transport properties is still debated. Here, we focus on $Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$ ($0 \leq x \leq 3$) NASICON electrolyte to elucidate the role of polyanion mixing on Na-transport properties. Although there is a large body of data available on this NASICON system, transport properties extracted from experiments or theory vary by orders of magnitude, signifying the need to bridge the gap between different studies. Here, more than 2,000 distinct ab initio-based kinetic Monte Carlo simulations have been used to map the statistically vast compositional space of NASICON over an unprecedented time range and spatial resolution and across a range of temperatures. We performed impedance spectroscopy of samples with varying Na compositions revealing that the highest ionic conductivity (~ 0.1 S cm^{-1}) is achieved in $Na_{3.4}Zr_2Si_{2.4}P_{0.6}O_{12}$, in line with our predictions (~ 0.2 S cm^{-1}). Our predictions indicate that suitably doped NASICON compositions, especially with high silicon content, can achieve high Na^+ mobilities. Our findings are relevant for the optimization of mixed polyanion solid electrolytes and electrodes, including sulfide-based polyanion frameworks, which are known for their superior ionic conductivities.