

Lithium Conductivity and Connectivity in (Li,Al)-Doped MgAl_2O_4 Spinel Electrolytes

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Lithium-ion batteries are well established in the portable electronics market as energy storage solutions. However conventional Li-batteries use liquid organic-polymer electrolytes, which are thermally unstable. Replacing these liquid organic electrolytes with electrochemically stable and non-flammable inorganic ceramic electrolytes would allow the construction of all-solid-state Li-batteries with improved safety and durability. While commercial use of solid-state electrolytes is impeded by their typical low ionic conductivity, it is not simply limited by bulk electrolyte conductivity: Li-batteries have multiple components (anode | electrolyte | cathode), and device performance depends on the rate of lithium transport between the electrolyte and electrodes.

One strategy to address this issue is to select electrode and electrolyte materials with a common crystal lattice structure, and matched lattice parameters^[1], thereby providing aligned diffusion pathways and potentially fast ionic transport through the device. Spinel structured electrodes are already used in commercial batteries, e.g. LiMn_2O_4 (cathode) and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (anode), and recently a new class of spinel structured lithium-ion conductors based on (Li,Al)-doped MgAl_2O_4 has been synthesised^[2].

Ionic conductivity within the doped spinel structured electrolytes will depend upon dopant concentration, cation site inversion, disorder and clustering, as well as the connectivity of lithium-ion sites in the equilibrated structures. Experimental work has shown that (Li,Al)-doped MgAl_2O_4 spinels have a low Li-ion conductivity^[3], emphasising the complexity of the structure and a need to understand the origin of this poor conductivity.

In this work we have developed polarisable-ion interatomic potentials, by carefully fitting to ab-initio forces, dipoles and stresses calculated for thermally distorted spinel electrolyte structures. Combining crystal connectivity analysis with long length and time scale molecular dynamics simulations performed with these potentials we explain the origin of the poor Li-ion conductivity, and suggest a potential route to improving it.

References:

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