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The diffusion of Na+ on modified NaSICON: a DFT investigation

Laura Gueci[1], Ph.D. Marco Bertini[1], MSc Ludovico Guercio[1], Prof. Francesco Ferrante[1], Prof. Dario Duca[1]
[1]Università degli Studi di Palermo

ORCID

https://orcid.org/0000-0002-7837-2037

NaSICON ionic superconductors, with the general formula NaxMM'(XO4)3 (where M, M' = {Fe, V, Ti, Zr, Sc, Mn, Nb, In} and X = {S, P, Si, As}), consist of octahedral MO6 and M'O6 units connected to three tetrahedral XO4 units. The first synthesized structure was Na1+xZr2SixP3−xO12 ($0 \leq x \leq 3$), from which non-stoichiometric variants like Na3+4y-xZr2-ySi2-xP1+xO12 can be derived, showing sodium and zirconium vacancies. Despite advances in powerful hardware and algorithms enabling atomistic calculations on complex systems, NaSICONs with non-unitary site occupancy of crystalline sites remain challenging, as stochastic site occupancy disrupts periodicity, requiring large supercells for precise electronic structure calculations. This is critical, because sodium ion migration energy is highly sensitive to the ions encountered along the diffusion path. In this work, DFT calculations were carried out on a supercell containing nearly 700 atoms, isolating the effects of site occupancy on sodium diffusion activation barriers as well as those of the consequent geometric distortions of the first coordination sphere around the sodium site. The analysis focused on a reference NaSICON and four derivative systems: one with a sodium vacancy, one with both a sodium vacancy and a silicon-to-phosphorus substitution, one with two Si/P substitutions, and one where all three silicon atoms in the migration channel were replaced by phosphorus. The lowest activation energy for Na+ diffusion was found to be 3.4 kJ/mol, significantly lower than values reported in the literature for similar systems, while the highest value was 19.9 kJ/mol. The study showed that dispersed Si/P substitutions enhance sodium diffusion. The supercell model employed ensures accurate results, which can be applied to statistical simulations of the diffusion process, and can be used for further studies of potential modifications to the NaSICON system, such as substituting zirconium with other metals, with the final purpose of obtaining systems featuring controlled electrolytic conductance behaviour.