

Theoretical Survey of Doped Na_xCoO_2 for Energy Conversion and Storage Applications

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Abstract

Doped sodium cobaltate (Na_xCoO_2) is suitable for highly efficient thermoelectric waste heat harvesting at temperatures around ~ 1000 K. This material is also a popular cathode for Na ion batteries. Due to the complex lattice structure and strong electronic correlation effects, atomistic understanding of the dopant's influence on the thermoelectric performance is challenging to resolve experimentally. In this work, we present a theoretical survey of 14 dopants in Na_xCoO_2 . After comparing with experimental results, we realise that dopants that substitute for a Na in the host lattice, such as Cu^{2+} , generally improve carrier mobility. However, if Na replacing dopants have an oxidation state larger than two, such as Eu^{3+} , electron-hole recombination severely reduces the carrier concentration, which is detrimental to thermoelectric performance. Moreover, a dopant with an oxidation state of +4 that replaces Co in the host lattice, such as Sn^{4+} , generally raises the Seebeck coefficient. Furthermore, in the case of dopants adopting higher oxidation state, such as Sb^{5+} , the strong electrostatic repulsion against Na ions decreases the electrochemical potential of Na extraction which leads to lower operating voltage if used as a cathode for Na ion batteries. We examined a wide range of dopants and their effect on the electronic structures of Na_xCoO_2 using density functional method. We found that some dopants like Mg, Ba, Sr, Au and Eu tend to substitute for a Na ion for a wide range of Na concentrations (x). In contrast, some other dopants like Ni, Bi, W, Sb and Sn tend to be more stable when substituting Co. The incorporation site of dopants such as Au and Y and Cu, however, strongly depends on Na concentration. In the case of Mg_{Na} , we could experimentally verify Mg's local chemical environment using Raman spectroscopy validating the theoretical results

References

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