Computer Simulation and Phase Diagram Prediction of $Li_2S_{1-x}Se_x$ Systems

Cliffton M. Masedi[a,b] , Happy M. Sithole[2] and Phuti E Ngoepe[1]

[1] *Materials Modelling Centre, University of Limpopo, Private Bag x1106, Sovenga, 0727, South Africa.*
[2]*Centre for High Performance Computing, CSIR, PO Box 392, Pretoria, 0001*

Lithium-sulfur (Li-S) batteries are an attractive Li-ion alternative that provides large capacity (1672 $mAhg^{-1}$) and energy density (2500 $Wh\ kg^{-1}$) while also being low cost, earth-abundant, and lightweight [1–3]. Li/S suffers from the low conductivity of S and the solubility of intermediary polysulfide species during cycling. It has been reported that Se and mixed Se_xS_y represent an attractive new class of cathode materials with promising electrochemical performance in reactions with both Li and Na ions [4]. Notably, unlike existing Li/S batteries that only operate at high temperature, these new Se and Li/Se_xS_y electrodes are capable of room temperature cycling. In order to study large systems and impact of temperature effectively, empirical interatomic potentials of Li_2S and Li_2Se were derived and validated against available experimental and calculated structure, elastic properties and phonon spectra. In addition, complex high temperature transformations and melting of Li_2S and Li_2Se were reproduced, as deduced from molecular dynamics simulations. Furthermore, cluster expansion and Monte-Carlo simulations were employed to determine phase changes and high temperature properties of mixed Li_2S-Se. The former generated 42 new stable multi-component Li_2S-Se structures and ranked metastable structures by enthalpy of formation. Monte Carlo simulations produced thermodynamic properties of Li_2S-Se system for the entire range of Se concentrations obtained from cluster expansion and it demonstrated that Li_2S-Se is a phase separating system at 0K but changes to mixed system at approximately 350K which was confirmed by constructed by phase diagram of Li_2S-Se system. It was finally demonstrated that molecular dynamics and Monte Carlo simulations techniques yield consistent results on phase separation and high temperature behavior of Li_2S-Se at 50% of sulphur and selenium.

References:

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