First Principles Comparative Study of Lithium, Sodium, and Magnesium Storage in Pure and Gallium-Doped Germanium: Competition between Interstitial and Substitutional Sites

National Univ. of Singapore¹, (present address) CEA Grenoble², °Sergei Manzhos¹, Fleur Legrain^{1,2} E-mail: mpemanzh@nus.edu.sg

Electrochemical batteries are believed to be a key technology to decarbonize transportation and electricity supply. Na and Mg ion batteries have emerged as promising alternatives to the widely used Li ion batteries. An anode material which would provide simultaneously a high energy density, a good rate capability, and a high cycle life has not yet emerged neither for Na- nor for Mg-ion batteries. Here, we investigate germanium which has been shown to be a promising material for Na ion as well as Li ion batteries. Compared to Si, Ge provides higher ionic diffusivities and more stable insertion sites for Li/Na/Mg (i.e. intercalation of Na and Mg can be easier in Ge compared to Si), and its isotropic expansion can reduce the mechanical stresses generated during intercalation compared to the anisotropic swelling of Si. It is well established that Li doping of Si results in interstitial Li defects. This is apparently also true for Na insertion. Mg impurities in Ge were previously attributed to substitutional defects. This suggests that Ge may possess more favorable insertion energetics for substitutional defects than for interstitial. This is important for potential use of Ge in electrochemical batteries, as it would strongly affect both voltages and rate capability, as voltage is directly related to defect formation (insertion) energy, and rate capability directly related to diffusion barriers which are defect type dependent. It is therefore important to understand the thermodynamics and kinetics of insertion of Li, Na, and Mg into Ge at different types of sites.

We present a comparative computational study of the insertion and diffusion of Li, Na, and Mg in Ge at different concentrations at substitutional and interstitial sites. We find that, depending on the concentration, the most stable configurations for Li, Na, and Mg insertion can consist of tetrahedral sites, substitutional sites, or a combination of the two types of sites. This is an important finding, as most of the previous ab initio studies of alloying type electrode materials ignored substitutional sites. The defect formation energies computed at dilute concentration (x = 1/64) show that Na and Mg insertion are not thermodynamically favored in Ge vs formation of bulk Na and Mg, as opposed to Li insertion which is favored. We show that a larger mechanical stress generated by Na and Mg insertion, compared to Li insertion, contributes to the high energy cost of insertion. We investigate the effect of p doping of Ge (with Ga) on the thermodynamics and find that it considerably lowers the defect formation energies associated with the insertion of Li/Na/Mg at tetrahedral sites. On the other hand, the energetics associated with Li/Na/Mg insertion at substitutional sites are not significantly affected. In addition, we compute the migration energy barriers for Li/Na/Mg diffusion between two tetrahedral sites (0.38/0.79/0.66 eV), between two substitutional sites (1.11/1.20/2.14 eV), and between two sites of different type (2.15/1.78/0.85 eV).