Alpha-Sn versus Beta-Sn Anodes for Li-, Na-, and Mg-ion Batteries: a First-Principles Study Including the Effect of Phonons

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Tin is extensively researched as anode material for Li, Na, and Mg ion batteries. Initial stages of charge proceed via solid solution and affect relative phase stability of α vs β Sn. We present a comparative ab initio study of Li, Na, and Mg insertion α and β Sn, including phononic effects. Mg doping at low concentration is found to stabilize the β phase. On the contrary, Li and Na doping is shown to reverse the stability of the phases at room temperature: Li/Na-doped α-Sn is more stable than Li/Na-doped β-Sn up to a temperature of around 380/400 K (to compare to α–β transition temperature of ~290 K in pure Sn). This may rationalize the formation of α-Sn upon lithiation and delithiation of β-Sn anodes reported in experimental studies. The changes in phase stability with Li/Na/Mg doping are directly related to the intercalation energies of Li/Na/Mg in one phase versus the other: at 300 K, Li/Na is easier intercalated in α-Sn (-0.37/-0.08 eV, with negative values for thermodynamically favored insertion vs Li/Na bulk) than in β-Sn (0.06/0.49 eV), while Mg intercalation energy is, although positive (i.e. unfavored intercalation), lower in β-Sn (0.53 eV vs Mg bulk) than in α-Sn (0.66 eV). The temperature effect is found to affect significantly the intercalation energy, by up to 0.13 eV at 300 K. Analysis of diffusion barriers shows that Li, Na, and Mg diffusion in β-Sn is anisotropic with migration barriers along the (001) direction (respectively 0.01, 0.22, and 0.07 eV) significantly lower than those in α-Sn (respectively 0.20, 0.52, and 0.40 eV).

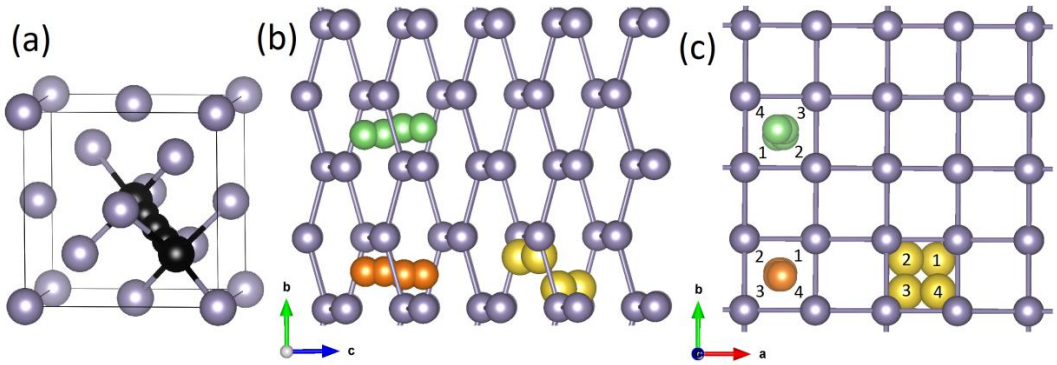

***Figure 1**. Insertion sites and migration pathways for Li/Na/Mg in α-Sn (a) and β-Sn (b, c). The larger black atoms show the equilibrium sites for Li/Na/Mg in α-Sn while the smaller black atoms lie along the migration pathways between two equilibrium sites; (b) and (c) Migration pathways for Li (green), Na (yellow), and Mg (orange) along the (001) direction in β-Sn (grey). (b) and (c) show the (100) and (001) planes, respectively.*