

Ab initio modeling of anode materials for Li, Na, and Mg ion batteries: post-Li issues, role of different phases, and computational matters

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The development of high capacity, high rate post-lithium (Na, Mg) ion batteries is a way towards wider use of renewable electricity. To this end, design of electrode materials with suitable storage energetics and diffusion properties is necessary. Our own and other labs' studies have shown that insertion of Na, Mg in some materials with great performance for Li ion batteries (such as crystalline Si) is often not favored thermodynamically and hindered kinetically. On the other hand, other materials might work for Li *and* Na or Mg, for example, Sn or TiO₂.

The (dis)charging of an electrode may cut across the phase diagram. Phases – both crystalline and amorphous - which are not thermodynamically most stable for the uncharged electrode at normal conditions may be stabilized by metal ion insertion or external conditions. We summarize our recent comparative computational studies of Li, Na, and Mg insertion into crystalline and amorphous (*a*-) Si, TiO₂ and Sn. We find that amorphous phases may be beneficial for Na and Mg storage in materials where storage in the most stable phase is inhibited. A number of insertion sites were identified in *a*-Si and *a*-TiO₂ where the defect formation energy for Li, Na and Mg is below that in crystalline phases and is negative (favored insertion). For example, the defect formation energy of Na in *a*-Si is competitive with Na's cohesive energy while it is positive for diamond Si. We also find that Al doping can also be used to strengthen binding of metal ions with the Si host and that Al-doped Si might work as anode for Na and Mg ion batteries.

For Sn, experiments reported formation and even dominance of the α phase upon charge-discharge, even though β -Sn is the more stable phase under normal conditions. We compute relative storage energetics of Li, Na, and Mg in α - and β -Sn and find that β -Sn does not thermodynamically favor insertion while α -Sn does (for Li and Na).

We will also discuss methodological issues we encountered when modeling the above materials at the DFT level. For example, we find wide variability in results with different DFT setups typically used in the literature, including qualitative differences when modeling insertion into Sn. For TiO₂, we find charge spin localization at the GGA level for which it was previously proposed that +U is required.

The speaker

Dr. Sergei Manzhos is currently Assistant Professor at the Department of Mechanical Engineering, National University of Singapore (NUS). His research interests are focused on the modelling of materials for electrochemical batteries, photoelectrochemical cells, and catalysis. He is also active in method developments in the areas of molecular and quantum dynamics. He holds a Ph.D. (Queen's U, 2005) in chemistry and an M.Sc. in radio physics (Kharkiv Ntl U, 1999). After a postdoc stint at the University of Montreal (2004-2008), he worked as Assistant Professor at the University of Tokyo (2008-20012) before joining NUS in 2012.