Theoretical study for lithium diffusion in $Li_2Ti_xO_y$ compounds

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Abstract

The structural properties, energetics and mobility of Li^+ in lithium containing titanates (Li_2TiO_3 and $Li_2Ti_3O_7$) are investigated theoretically with periodic quantum-chemical methods. The calculated electric field gradient (EFG) of β-Li_2TiO_3 reveals that there are three inequivalent Li sites (Li(1), Li(2) and Li(3)) and two inequivalent Ti sites (Ti(1) and Ti(2)). A honeycomb structure of LiTi2 is formed by the sharing of Ti ions and Li(3) ions. The rest of the lithium ions ((Li(1) and Li(2)) form pure lithium layers in between the $LiTi_2$ layers. The calculated Li vacancy formation energy shows that vacancy formation at the Li(3) sites is easier than those in Li(1) and Li(2) sites. Competing pathways for Li diffusion in β-Li_2TiO_3 are investigated using the climbing-image Nudged-Elastic-Band (cNEB) approach. Li^+ ions can migrate either along the crystallographic *c* direction or within the crystallographic *ab* plane. Our calculated activation energy (E_A) in the *ab* plane ranges between 0.53 and 0.78 eV, whereas E_A along the *c* direction is 0.54 eV which are in the range of experimental E_A value (0.47 to 0.80 eV) for β-Li_2TiO_3.

The structure obtained according to the XRD analysis shows that the unit cell of $Li_2Ti_3O_7$ contains 4 formula units of $Li_3Ti_1O_2$ with Li:Ti:O stoichiometric ratio 3:1:2. However, in $Li_2Ti_3O_7$, the real stoichiometry of Li:Ti:O is 2:3:7. In the present study, the structure elucidation with correct stoichiometric ratio is performed for the first time. The relative stability of various considered models is evaluated on the structurally optimized structures. It is observed that the stability varied between 0–8 eV for all the considered structures. The most stable models are then employed for the investigation of Li^+ diffusion processes. Li^+ can migrate along the 'one dimensional channel' from one occupied tetrahedral site to another unoccupied tetrahedral site or along crystallographic *ac* plane from the occupied tetrahedral sites to the empty octahedral locations. Our calculated E_A for Li^+ diffusion in the one dimensional channel ranges from 0.67 to 0.72 eV and that in the *ac* plane ranges from 0.50 to 0.80 eV. These are in well accord with the available experiment.

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