batteries

MDPI

Supplementary Information

DFT Modelling of $Li_6SiO_4Cl_2$ Electrolyte Material for Li-ion Batteries

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The following equation combines formation energies of a Li vacancy and a Li interstitial to calculate the formation energy of Li Frenkel pair (FP_{Li}). Similar equations were used for other Frenkel pairs.

$$E_{for}(FP_{Li}) = E_{for}(V'_{Li}) + E_{for}(Li^{\bullet}_{i}) \quad (1)$$

Formation energies of Schottky and anti-site defects were calculated using the following equations.

$$E_{for}(\text{Schottky}) = 6\,E\,[V'_{Li}]_{1\times2\times2} + E\,[V''''_{Si}]_{1\times2\times2} + 4\,E\,[V^{\bullet\bullet}_{O}]_{1\times2\times2} + 2\,E\,[V^{\bullet}_{Cl}]_{1\times2\times2}\,E[Li_6SiO_4Cl_2] - 13\,E[Li_6SiO_4Cl_2]_{1\times2\times2} \quad (2)$$

$$E_{for}(Li_2O\ \text{Schottky}) = 2\,E\,[V'_{Li}]_{1\times2\times2} + E\,[V^{\bullet\bullet}_{O}]_{1\times2\times2} + E(Li_2O) - 3\,E[Li_6SiO_4Cl_2]_{1\times2\times2} \quad (3)$$

$$E_{for}(\text{LiCl Schottky}) = E\,[V'_{Li}]_{1\times2\times2} + E\,[V^{\bullet}_{Cl}]_{1\times2\times2} + E(\text{LiCl}) - 2\,E[Li_6SiO_4Cl_2]_{1\times2\times2} \quad (4)$$

$$E_{for}(SiO_2\text{Schottky}) = E\,[V''''_{Si}]_{1\times2\times2} + 2\,E\,[V^{\bullet\bullet}_{O}]_{1\times2\times2} + E(SiO_2) - 3\,E[Li_6SiO_4Cl_2]_{1\times2\times2} \quad (5)$$

$$E_{for}(O/Cl\ \text{anti}-\text{site})(\text{isolated}) = E\,[O'_{Cl}]_{1\times2\times2} + E\,[Cl^{\bullet}_{O}]_{1\times2\times2} - 2\,E[Li_6SiO_4Cl_2]_{1\times2\times2} \quad (6)$$

$$E_{for}(O/Cl\ \text{anti}-\text{site})(\text{cluster}) = E\,[O'_{Cl}{:}\,Cl^{\bullet}_{O}]_{1\times2\times2} - E[Li_6SiO_4Cl_2]_{1\times2\times2} \quad (7)$$

where $E\,[V'_{Li}]_{1\times2\times2}$, $E\,[V''''_{Si}]_{1\times2\times2}$, $E\,[V^{\bullet\bullet}_{O}]_{1\times2\times2}$ and $E\,[V^{\bullet}_{Cl}]_{1\times2\times2}$ are the total energies of a 1×2×2 supercell consisting of a single Li, Si, O and Cl vacancy respectively. $E\,[O'_{Cl}]_{1\times2\times2}$ and $E\,[Cl^{\bullet}_{O}]_{1\times2\times2}$ are the total energies of a 1×2×2 supercell consisting of O'_{Cl} and $Cl^{\bullet}_{O}$ defects respectively. $E[Li_6SiO_4Cl_2]_{1\times2\times2}$ is the total energy of a 1×2×2 supercell. $E[Li_6SiO_4Cl_2]$ is the total energy per for mula unit of $Li_6SiO_4Cl_2$.

Table S1. Total energies of point defects calculated in the 1 × 2 × 2 supercell.

Defect	Total energy (eV)
Vacancies	
V_{Li} (1)	–1132.45
V_{Li} (2)	–1132.45
V_{Li} (3)	–1132.45
V_{Li} (4)	–1132.38
V_{Li} (5)	**–1132.50**
V_{Li} (6)	–1132.50
V_{O} (1)	**–1127.85**
V_{O} (2)	–1127.85
V_{O} (3)	–1127.85
V_{O} (4)	–1132.85
V_{Si} (1)	**–1118.17**
V_{Cl} (1)	**–1132.32**
V_{Cl} (2)	–1132.32
Interstitials	
Li_i (1)	–1138.96
Li_i (2)	**–1138.96**
Li_i (3)	–1138.72
Li_i (4)	–1138.91
Li_i (5)	–1138.39
Li_i (6)	–1138.90
O_i (1)	–1142.75
O_i (2)	–1142.68
O_i (3)	–1142.84
O_i (4)	–1141.49
O_i (5)	**–1142.91**
Cl_i (1)	**–1138.98**
Cl_i (2)	–1139.92
Cl_i (3)	–1138.74
Cl_i (4)	–1138.23
Si_i (1)	**–1139.34**
Si_i (2)	–1138.31
Si_i (3)	–1139.14
Si_i (4)	–1139.23

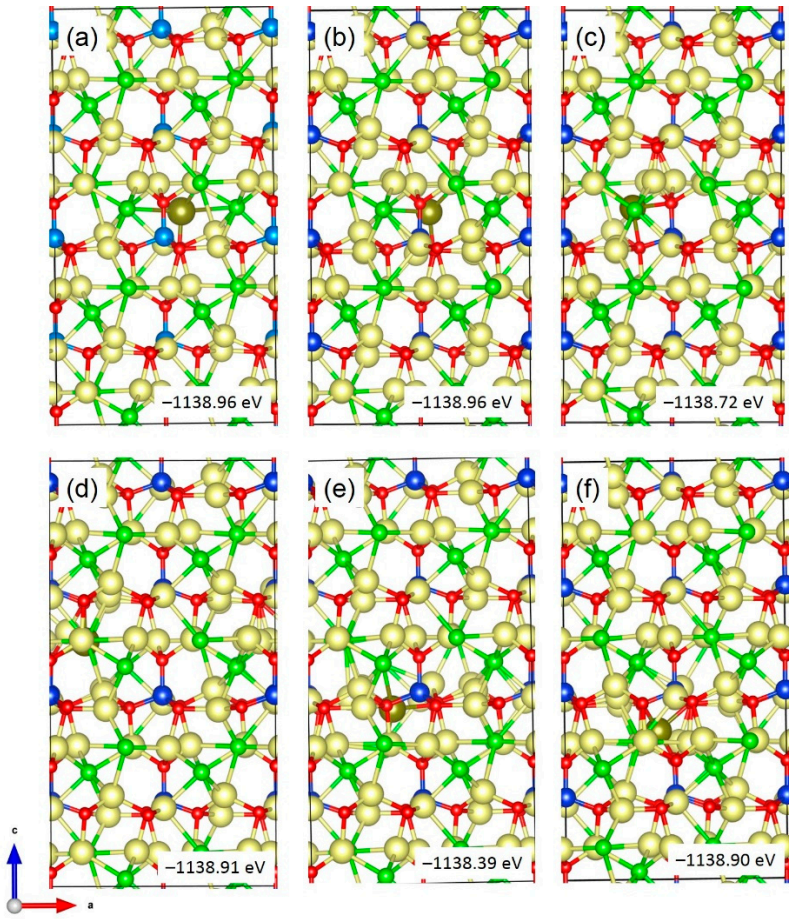

Figure S1. (a–f) Different configurations of a single Li incorporated into $Li_6SiO_4Cl_2$.

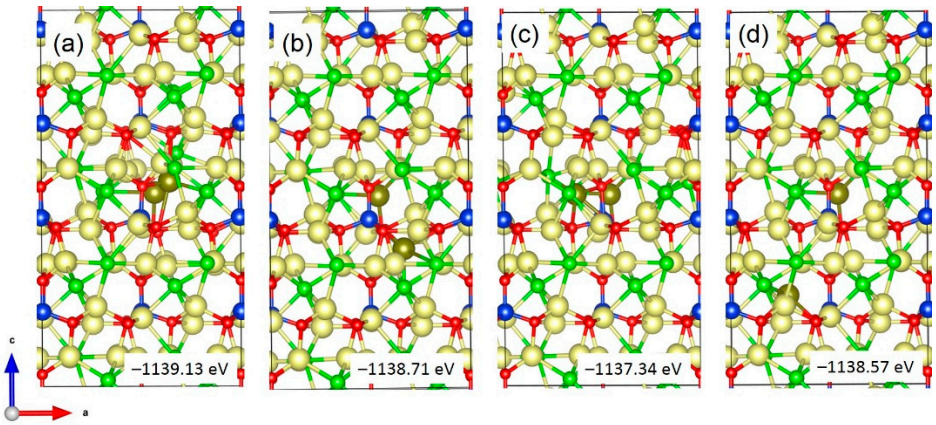

Figure S2. (a–d) Different configurations of two Li atoms incorporated into $Li_6SiO_4Cl_2$.

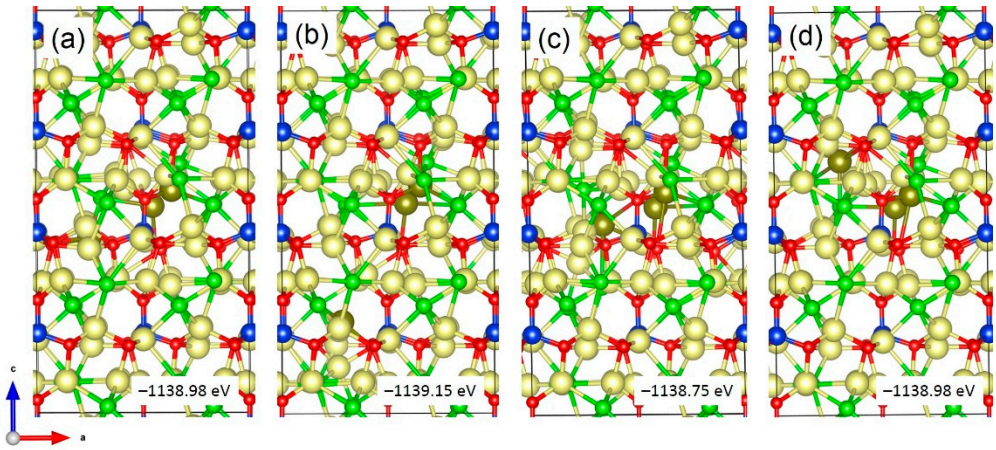

Figure S3. (a–d) Different configurations of three Li atoms incorporated into $Li_6SiO_4Cl_2$.