Mechanistic study in delithiations of sulfur-substituted Li$_2$FeSiO$_4$ by first-principles calculations

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The first-principles calculations were performed to investigate the structural, electronic and electrochemical characteristics of Li$_2$FeSiO$_4$ and S-substituted Li$_2$FeSiO$_4$. The feasibility in removal of two Li ions from the proposed Li$_2$FeSiO$_4$S is further explored. The calculated results reveal that the delithiation paths of Li$_2$FeSiO$_4$ are significantly modified by substitution of an O with an S ion because of larger S radius. The bond lengths between Li-O and Li-S become longer and the gaps between the pseudo-layers [Fe$_2$Si$_2$O$_6$S$_2$]$_\infty$ becomes wider, leading to lower deintercalation voltages and minor structural deformations in Li$_2$FeSiO$_4$S. The extraction of the first Li ion involves Fe$^{2+}$/Fe$^{3+}$ for both Li$_2$FeSiO$_4$ and Li$_2$FeSiO$_4$S, thus, the deintercalation voltage of Li$_2$FeSiO$_4$S reduces to 2.90 V with a slight expansion of 4.0% in cell volume. However, the extraction of the second Li ion in Li$_2$FeSiO$_4$ corresponds to a combined redox couple of Fe$^{3+}$/Fe$^{4-}$ and O$^{2-}$/O$^{-\alpha}$ (0<$\alpha$<1 and 1<$\gamma$<2), which results in not only a large deintercalation voltage of 4.85 V, but also a large volume expansion of 11.5%. The hypothermal Li$_2$FeSiO$_4$S lowers the deintercalation voltage to 4.19 V with a new redox reaction of S$^{2-}$/S and a slight reduction of 2.3% in cell volume. Ultimately, a full extraction of two Li ions can be realized by Li$_2$FeSiO$_4$S in current conventional electrolytes.