

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

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The first-principles calculations were performed to investigate the structural, electronic and electrochemical characteristics of $\text{Li}_2\text{FeSiO}_4$ and S-substituted $\text{Li}_2\text{FeSiO}_4$. The feasibility in removal of two Li ions from the proposed $\text{Li}_2\text{FeSiO}_3\text{S}$ is further explored. The calculated results reveal that the delithiation paths of $\text{Li}_2\text{FeSiO}_4$ 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 $[\text{Fe}_2\text{Si}_2\text{O}_6\text{S}_2]_\infty$ becomes wider, leading to lower deintercalation voltages and minor structural deformations in $\text{Li}_2\text{FeSiO}_3\text{S}$. The extraction of the first Li ion involves $\text{Fe}^{2+}/\text{Fe}^{3+}$ for both $\text{Li}_2\text{FeSiO}_4$ and $\text{Li}_2\text{FeSiO}_3\text{S}$, thus, the deintercalation voltage of $\text{Li}_2\text{FeSiO}_3\text{S}$ reduces to 2.90 V with a slight expansion of 4.0% in cell volume. However, the extraction of the second Li ion in $\text{Li}_2\text{FeSiO}_4$ corresponds to a combined redox couple of $\text{Fe}^{3+}/\text{Fe}^{(4-\alpha)+}$ and $\text{O}^{2-}/\text{O}^{\alpha-}$ ($0 < \alpha < 1$ and $1 < \alpha < 2$), which results in not only a large deintercalation voltage of 4.85 V, but also a large volume expansion of 11.5%. The hypothermal $\text{Li}_2\text{FeSiO}_3\text{S}$ 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 $\text{Li}_2\text{FeSiO}_3\text{S}$ in current conventional electrolytes.