

Role of asymmetry in the physicochemical and electrochemical behaviors of perfluorinated sulfonimide anions for lithium batteries: A DFT study

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Highlights

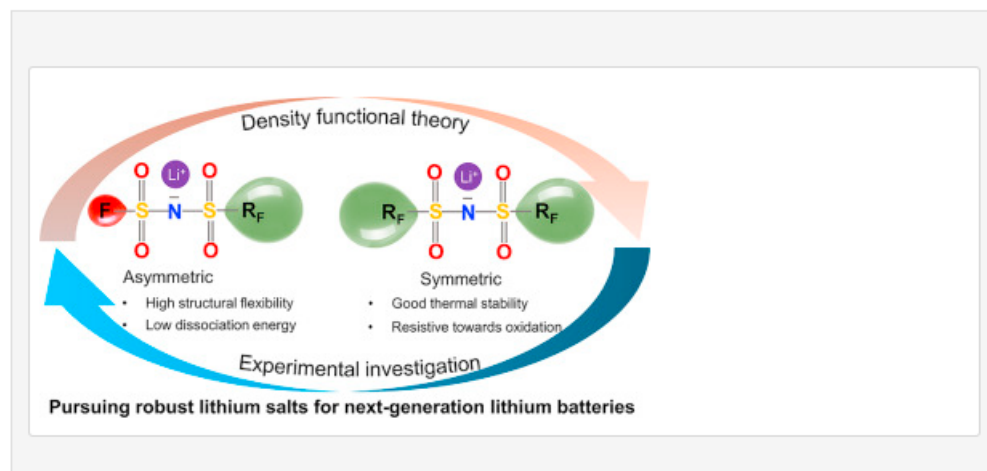
- DFT calculations of perfluorinated sulfonimide anions (PSAs) are presented.
- Good internal flexibility of the S–N bond in asymmetric PSAs.
- Asymmetric PSAs have lower lithium dissociation energy.

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Abstract

Lithium salts based on perfluorinated sulfonimide anions (PSAs) are promising new electrolyte components for application in next-generation lithium batteries. Several typical symmetric ($[(n-C_mF_{2m+1}SO_2)_2N]^-$, $m = 0, 1, 2, 3$, and 4) and asymmetric ($[(FSO_2)(n-C_mF_{2m+1}SO_2)N]$, $m = 1, 2, 4, 6$, and 8) PSAs have been extensively investigated in recent years. Yet little is known about the role of asymmetry in the physicochemical and electrochemical properties at the molecular level. Here we use first-principle density functional theory calculations to thoroughly examine such fundamental structure-activity relationship. Compared to symmetric PSAs, asymmetric isomers show intrinsically better internal flexibility of the S–N bond, lower dissociation energy of Li^+ cation, and thereby they can be promising candidates for polymer electrolytes. We also observe that more than four C atoms in the perfluorinated chain results in negligible improvements in terms of dissociation energy, thermal stability, and anodic stability. These results provide an in-depth understanding of the impact of the molecular structure on PSAs, helping design new robust anions for lithium batteries in the future.

Graphical abstract



Keywords

Lithium batteries; Perfluorinated sulfonimide anions; Lithium salts; DFT calculation