Density Functional Theory based Electrolyte Design Formulation for Lithium-Sulfur Batteries

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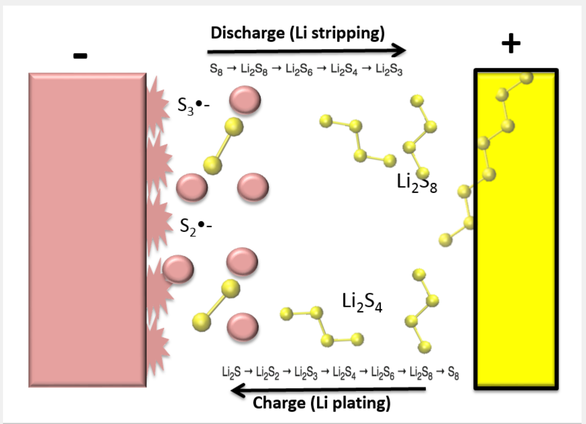
Background

Lithium-ion (Li-ion) batteries are commonly used in portable electronics (cellphones & laptops). Li-ion batteries have a theoretical specific energy of 400-600 Wh/kg while, comparably, lithium-sulfur (Li-S) batteries have demonstrated a much higher theoretical specific energy of 1550 Wh/Kg. Li-S batteries have the potential to be a powerful battery as well as an inexpensive one due to the relative abundance and low cost of sulfur.

Knowledge Gaps

The polysulfide “shuttle phenomenon” is due to the dissolution of sulfide from the cathode, causing aggregate precipitation of shuttled polysulfide species upon the anode. This results in corrosion and ultimate failure of the battery. Inhibiting this parasitic reaction is a major challenge for the viability of Li-S batteries.

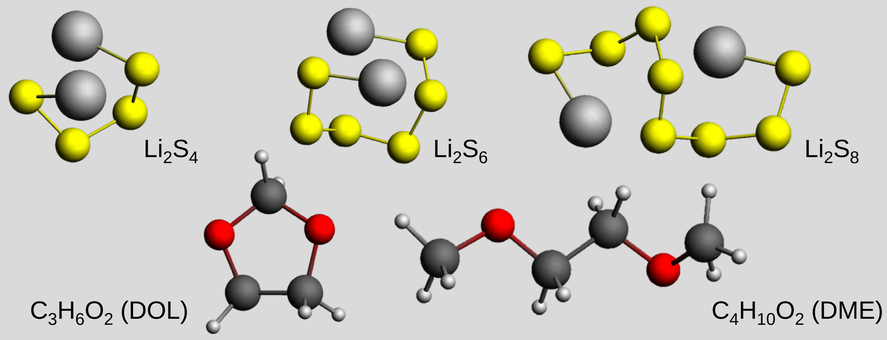


Objectives

To develop the next generation battery that is powerful yet cost-efficient. Understanding the molecular processes in the Li-S cell is the first step towards designing ways to mitigate the reactions that are not conducive to practical operation. Li-S battery performance can be subsequently improved by rational electrolyte design from understanding of solvate structure.

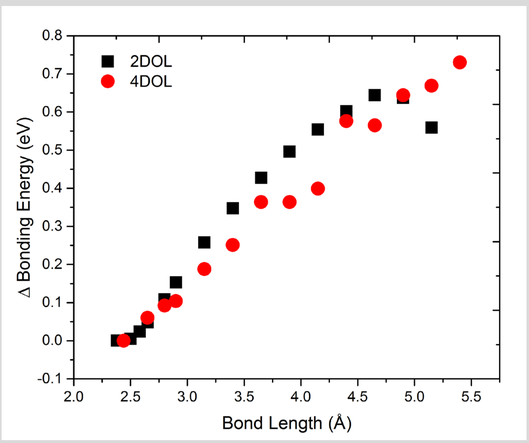
Methods & Materials

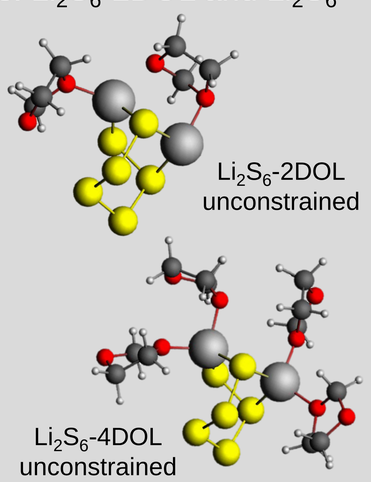
Computational modeling based on density functional theory (DFT) is used in the bonding energy analysis of sulfide solvate structures. The polysulfide structures studied in this research are Li_2S_n (n=4,6,8) interacting with solvent molecule 1,3-dioxolane (DOL) and dimethoxyethane (DME).



Interactions of DOL

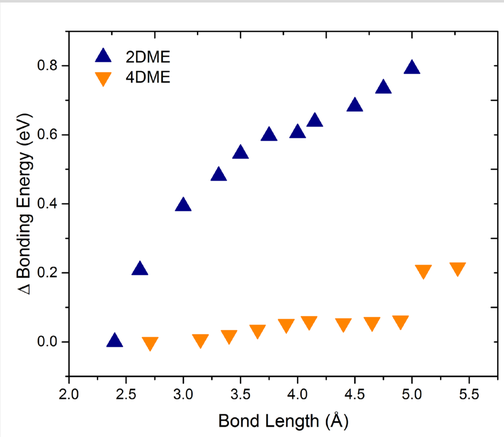
By constraining Li-S bond length, Li-DOL interaction strength is monitored during de-lithiation process. Li_2S_6-2DOL and Li_2S_6-4DOL have similar bonding energies

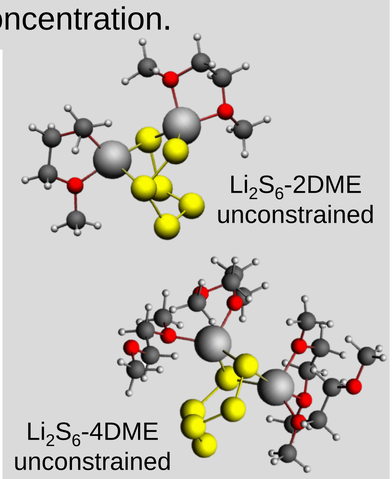




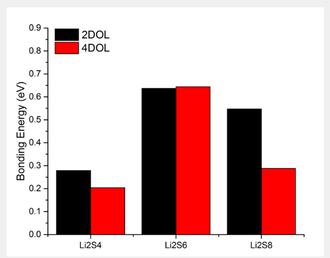
Interactions of DME

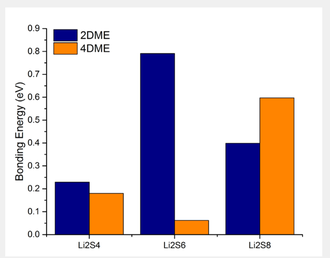
Similarly, by constraining Li-S bond length the Li-DME interaction strength is monitored during de-lithiation process. The bonding energies of Li_2S_6-2DME and Li_2S_6-4DME decrease with increase in solvent concentration.





Discussion





Sulfide to solvent ratio is critical in predicting polysulfide de-lithiation process in Li-S battery. Our results indicated that:

- Li_2S_6 shows higher de-lithiation energy than Li_2S_4 and Li_2S_8
- DOL concentration is not critical in de-lithiation of polysulfide molecules
- DME concentration might play a principal role in de-lithiation of polysulfide molecules

Further research into sulfide to solvent ratio can aid rational electrolyte design of Li-S battery.

Acknowledgements

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References

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- Sulfur image. Freeport Sulphur company.

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