First Principles Calculations of Existing and Novel Electrode Materials

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Project Bat054

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Overview

Timeline

- Start Date Oct 1 2016
- End Date: Sept 2020

Budget

- Total budget (4 years): $1,800K
- FY18 funding $450K

Barriers Addressed

- Solid-state conductors needed that combine good electrochemical properties with processability.
- Correlation between synthesis condition and performance of lithium-thio-sulphate conductors is unclear.

Partners/Collaborations within the VT program

Kristin Persson (LBNL), **NCEM** (LBNL)

Relevance: Solid-State Batteries

Impact:

- To make solid-state batteries we need conductors that combine good electrochemical properties with processability. Currently, solution-processed LPS conductors have lower conductivity than those made through solid-state (ball milling)
- By understanding the factors that control Li-ion motion in crystalline and amorphous solids we will be able to understand better how processing influences performance

Objectives:

- Understand the role of local structure on ionic conductivity and use to find the optimal amorphous LPS.
- Understand the interface reactivity of LPS with electrodes, and design suitable coating materials to avoid harmful interface reaction.
- Develop rational design principle to engineer the structure and composition of LPS electrolyte.

Approach

- Construct the Li-P-S phase diagram to understand stability of crystalline phase.
- Model amorphous LPS and identify the common local structure motifs and relate to ionic conductivity
- Identify suitable coating material to minimize the reaction between LPS and cathode during cycling

Methods

- DFT with GGA and SCAN functional for energy calculations. Molecular Dynamics for Li-transport
- Phonon calculations with harmonic approximation for vibrational contribution to free energy.
- Simulation of PDF and Raman/IR spectroscopy to capture the structural features of different LPS phases.
- High throughput computational study of reaction energy of coating materials with LPS.

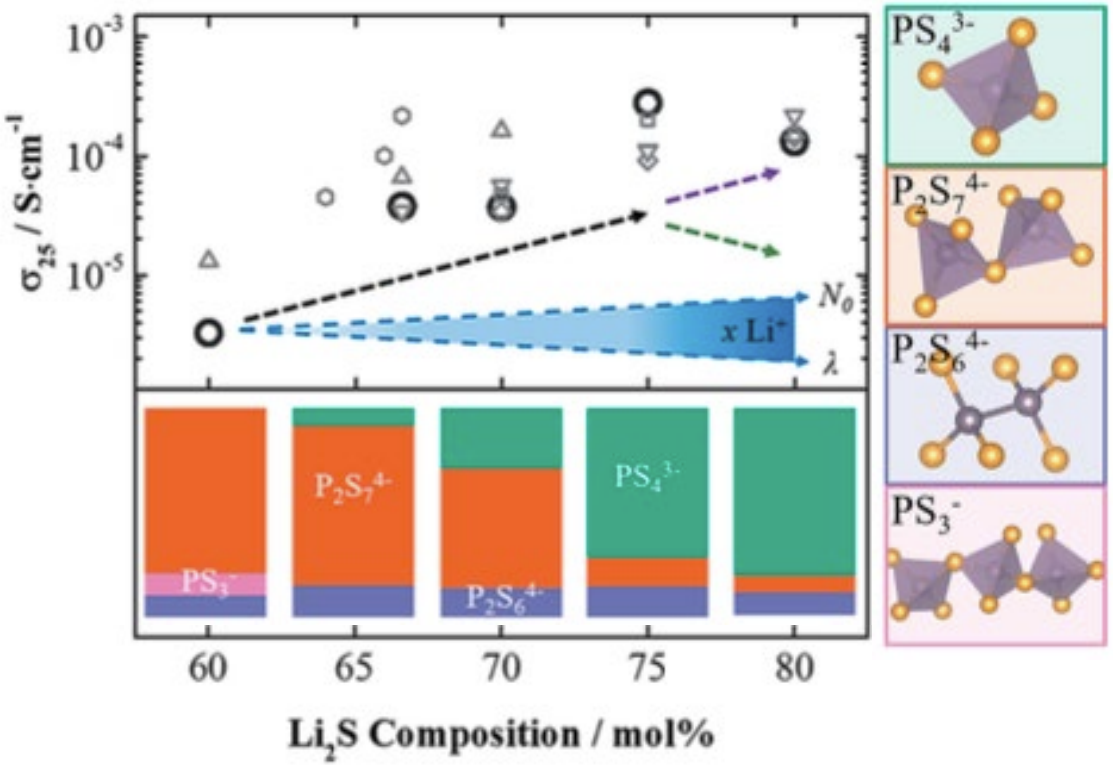
The conductivity of amorphous LPS correlates to its local structures

Different ionic conductivity for amorphous Li_3PS_4

- From suspension synthesis: 7.4×10^{-5} S cm^{-1}
- From ball-milling : 2.8×10^{-4} S cm^{-1}

The gap may come from different local structures of amorphous LPS

Different local structures (from ^{31}P MAS NMR) in glassy xLi_2S-$(1-x)P_2S_5$ from ball-milling:



Increase of conductivity cannot be explained solely by Li content increase, local anion species may also contribute.

Therefore, understanding the relation b/w the **structure** and **conductivity** of amorphous LPS is important.

Liu, Z. et al. J. Am. Chem. Soc. 135 (2013): 975–978.
Dietrich et al., J. Mater. Chem. A, 2017, 5, 18111–18119

Technical achievements: Accurate phase diagram for stability of crystalline phase

Stable Phase

Metastable Phase

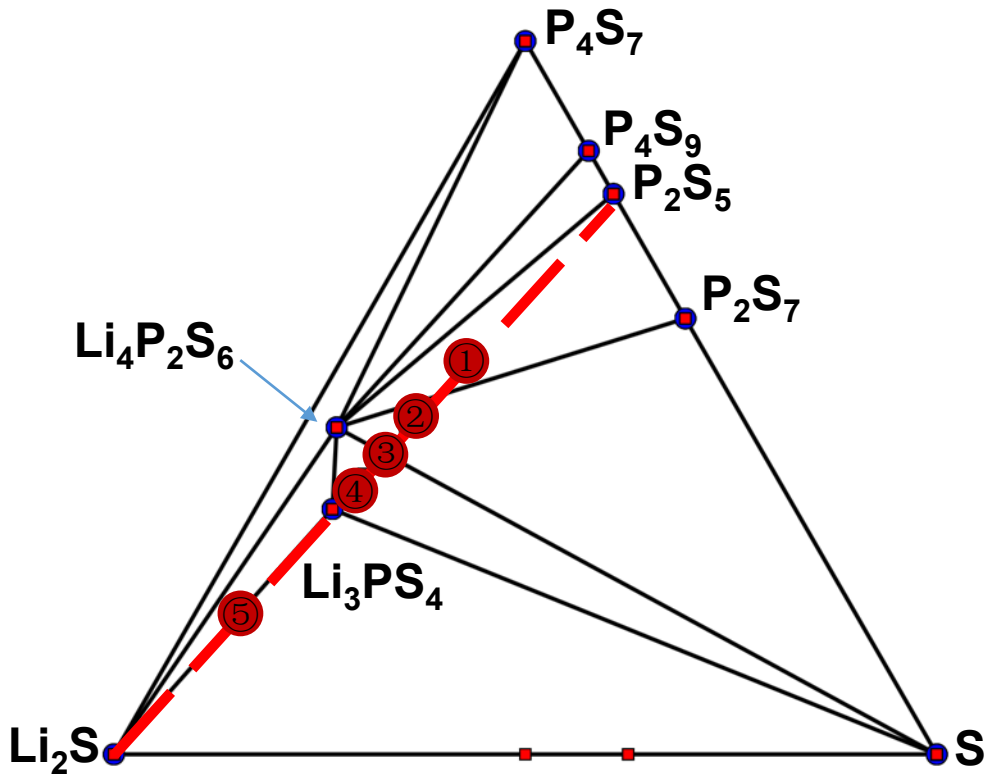
① **$LiPS_3$** (Li_2S+P_2S_5)

② **$Li_5P_3S_{10}$** (5Li_2S+3P_2S_5)

③ **$Li_4P_2S_7$** (2Li_2S+P_2S_5)

④ **$Li_7P_3S_{11}$** (7Li_2S+3P_2S_5)

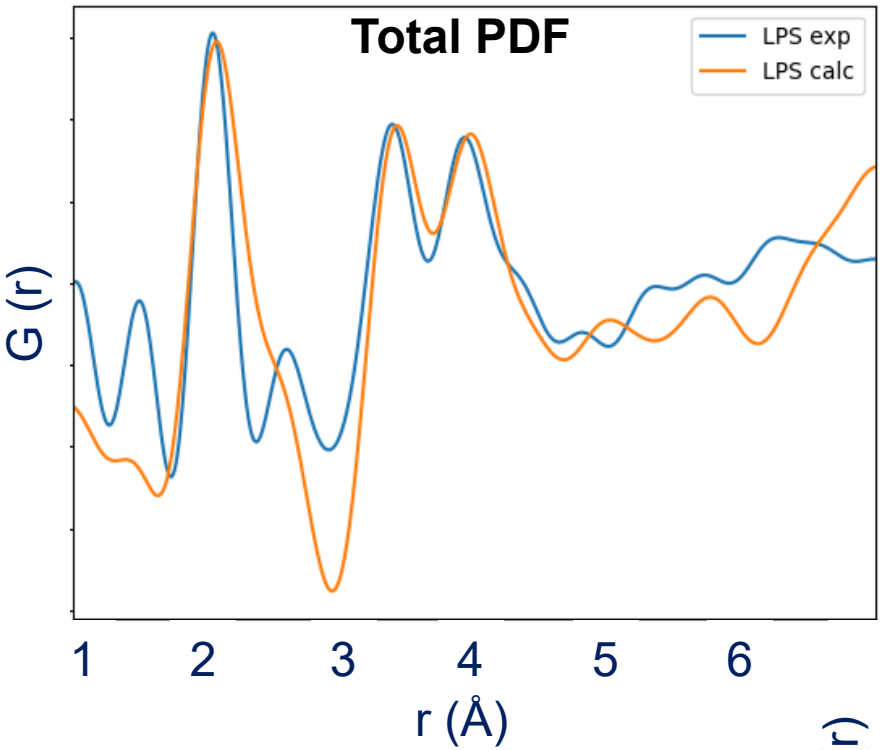
⑤ **Li_7PS_6** (7Li_2S+P_2S_5)

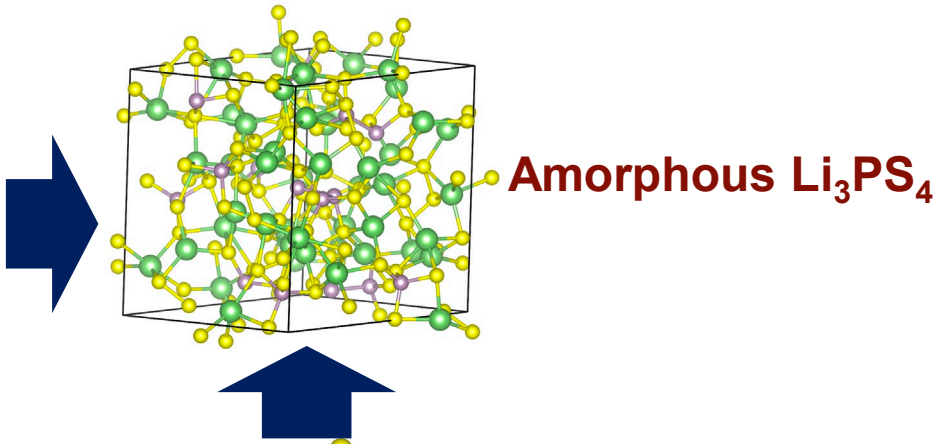


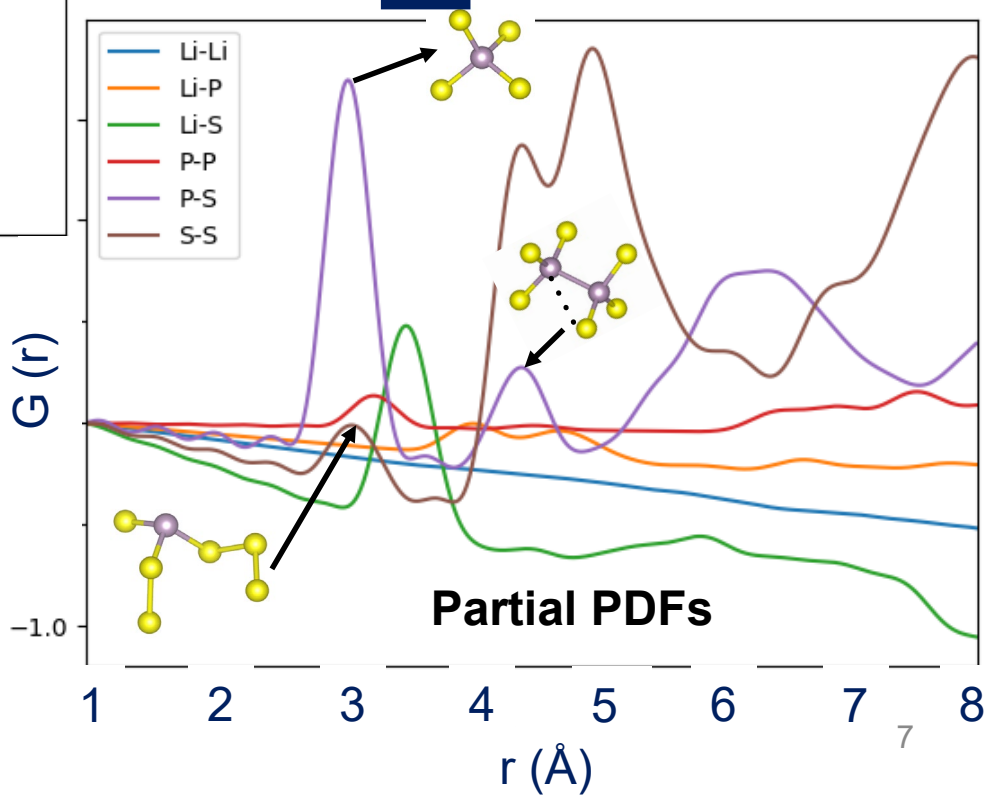
The SCAN-DFT computed phase diagram:

- Computed formation enthalpy in sulfides is consistent with experiments.
- SCAN-DFT designates correct phases as stable or metastable. This is a good basis on which to form the full temperature-dependent phase diagram

Technical achievements: Structural model for amorphous LPS from ab-initio Molecular Dynamics



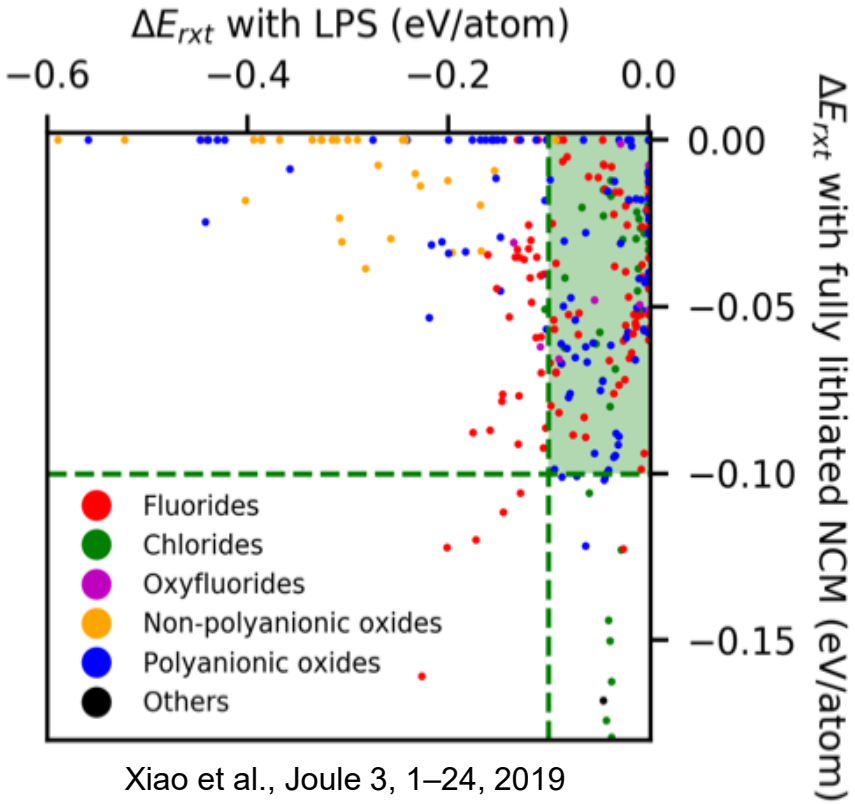




- The PDF from simulated amorphous LPS is consistent with experiments.
- “atypical” structural features exist in amorphous LPS and maybe important for ionic conductivity.

Technical achievements: Discovery of novel coating materials that stabilize LPS at interface

- High throughput interface reaction calculations are performed for screening potential coating materials for oxidation resistance and low reactivity with NMC cathode and LPS conductor
- The coating materials that also have good ionic conductivity are highlighted in red



Xiao et al., Joule 3, 1–24, 2019

Representative candidates that have good chemical stability with LPS:

Halides	Polyanionic Compounds	
$LiCsCl_2$	$LiCs(PO_3)_2$	**$LiPO_3$**
$LiRbCl_2$	$LiLa(PO_3)_4$	Li_3PO_4
$LiYF_4$	$LiBa(B_3O_5)_3$	**LiH_2PO_4**
$LiGaCl_4$	LiB_3O_5	**$LiTi_2(PO_4)_3$**
$LiBF_4$	$LiZr_2(PO_4)_3$	$LiY(PO_3)_4$

Proposed future work

Understand mechanism of ionic conductivity in amorphous LPS

- Motivation: Understand the influence of different local structures and correlate to processing
- Methods:
  - Ab initio Molecular dynamic simulation (AIMD) combined with short range ordering analysis and characterization simulation.
  - Correlate structural features with ionic conductivity and compare to experimental characterization of amorphous LPS

Develop rational design strategy for LPS with good ionic conductivity.

- Study the influence of the composition on amorphous LPS of different phases.
- AIMD simulations to obtain the evolution of conductivity of LPS at different compositions and phases.

Summary

Develop a in-depth understanding of LPS solid state electrolyte and rational design strategy is important to make new solid state batteries that can deliver high ionic conductivity steadily.

- We are advancing our understanding of the stability of different LPS phases with the tool of computational phase diagram.
- We have utilized high-throughput computation to identify potential coating materials to eliminate reaction of LPS with electrodes.
- We have developed a atomic-scale model that resolves the local structure of amorphous LPS and correlates well with different experimental characterizations(PDF, Raman/IR) .

Collaborations

- **Kristin Persson** (LBNL)
- **NCEM** (LBNL)

Response to Reviewers Comments

Not reviewed the previous year