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Influence of $Li_{10}GeP_2S_{12}$-type solid electrolyte on cell thermodynamics

Jishnu Bhattacharya[1] , C. Wolverton[2]

1) Mechanical Engineering Department, Indian Institute of Technology Kanpur, Kanpur, UP-208016, India.
2) Material Science and Engineering, Northwestern University, Evanston, IL-60208, USA

Abstract: We elucidate few critical facts about the lithium superionic conductor ($Li_{10}GeP_2S_{12}$) and few other compounds of the same family as the electrolyte in Li-ion cells. The dimensionality of diffusion process and existence of 'structural' lithiums are not well understood in this material. From the ab-initio MD simulations, we find that the material transport Li-ions predominantly in the crystallographic c-direction. Nevertheless, the cross-channel diffusion is significant as well. We explored the mobility of individual Li-ions and do not find evidence that supports the proposition of structural Li-ions in LGPS. We find nominal effect of local Ge-P ordering and of Li-concentration change on diffusivity, which not only provides information about the invariance of diffusivity at different conditions of operation, but also ensures that identification of the ground state structure in LGPS having partially occupied Li and Ge/P sublattices should have minimal effect on the diffusion analysis. We computed the dilute Li insertion and extraction voltages for LGPS from ab-initio total energy calculation. The dilute voltages indicate that the material is prone to react by exchanging Li-ions with the electrodes at typical operating range of voltages indicating formation of some interphase at the electrode-electrolyte interface, which necessitates further experimental investigation

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1. Introduction

This template, modified in MS Word 2007 and saved as a The recent discovery of crystalline $Li_{10}GeP_2S_{12}$ (LGPS), a lithium superionic conductor, as a solid state electrolyte for Li-ion batteries created significant interest as it showed remarkable room temperature ionic conductivity, even better than some ionic liquid electrolytes[1]. Kamaya et al. found LGPS to have a tetragonal crystal structure (space group 137) with a partially occupied Li-sublattice and diffusion to be occurring along one dimensional channels along the longer lattice direction (*c*-direction). They did not explicitly measure the conductivity along different crystallographic directions. They inferred the 1D Li-ion diffusion along the c-direction from the anisotropic character of the thermal vibrations.

After its discovery and characterization, several theoretical studies addressed various aspects of this material. Mo et al. studied this material from the first principles and found that it is not a ground state at 0 K.[2] They also found that the material has cross-channel diffusivity (in the *ab* plane) as opposed to 1D diffusion. While Kamaya et al. observed 1D Li-diffusion and Mo et al. found cross-channel Li jumps, Adams et al. (From molecular dynamics simulations) and Kuhn et al. (from thermal vibration analysis of single crystal structure X-ray diffraction data) found very weak anisotropy in Li diffusion in

LGPS indicating that the Li-ion diffusivities are not favoured in any particular crystallographic direction.[1-4] From DFT-based calculations, Ong et al. reported stability and conductivity of the family of materials with similar stoichiometry as $Li_{10}GeP_2S_{12}$.[5] They found the cation substitution of Si/Sn (for Ge) and Al (for P) has only a minimal effect on the phase stability and conductivity, which can effectively eliminate the use of expensive Ge from the composition of the solid electrolytes. They also found that oxide based compounds are less stable with respect to the T=0K phase diagram compared to the sulphides/selenides and the sulphides have larger Li-ion conductivity than both oxides and selenides.

The high Li-ion conductivity at room temperature certainly shows promise for the LGPS material to be a candidate solid electrolyte in future Li-ion batteries. Nevertheless, the material needs further investigation on several other aspects that are relevant for an electrolyte other than the ion conductivity. The dimensionality of diffusion pathway for the Li-ion is one of them. Whether diffusion occurs through one dimensional channels or there exists significant cross-channel diffusion is a matter of debate till date.[1, 2, 4, 6] If a material has purely 1 dimensional diffusion, some anti-site defect or other crystal defects may block such channels and diffusivity drops with repeated cycling leading to shorter life of the electrolyte. Existence of significant cross-channel diffusion alleviates this problem. Therefore it is important to gain understanding of the dimensionality of ion diffusivity in LGPS.

Kamaya et al. reported that in LGPS crystal, there are three types of Li sites at three Wyckoff sites: 16h, 8f and 4d.[1] They found that Li-ions only at the 16h and 8f sites participate in the diffusion process. Adams et al. studied the diffusion mechanism in LGPS from molecular dynamics simulations and proposed a paddle wheel mechanism including additional Li sites.[7] However they did not comment on how mobile the Li-ions at 4d sites are. Xu et al. also studied Li-ion diffusion in LGPS from ab-initio molecular dynamics but did not comment on the role of the Li-ions in the 4d sites.[6] To understand the diffusion mechanism in LGPS-type solid electrolytes and in designing new materials for that purpose, it is imperative to understand how mobile the Li-ions at different Wyckoff sites are relative to one another.

The Li sublattice is partially occupied in LGPS. During cell-operation, diffusive Li-ions can change the local concentration of Li. The charge neutrality requirement altered by the change of Li-concentration can alter the local Ge/P ratio and ordering as well. Whether Li-diffusivity is a strong function of the Li concentration changes as well as the alterations of the Ge/P ordering is important as to estimate if there is any critical concentration range (or ordering) that can be particularly rate-limiting during cell operation.

The true thermodynamic limit of the cell potential where LGPS can be used reversibly depend on the potentials at which LGPS actively participate in the electrochemical process of consuming/releasing Li ions changing its bulk composition. The voltages at which a material starts accepting or rejecting Li (i.e. dilute Li insertion/extraction voltages) indicate the limit of voltages where the material starts reacting with Li-ions as an electrode. Within the dilute voltage window, electrolyte will not react with cathode or anode by accepting or rejecting Li ions (altering its own composition). However, using an electrolyte outside its dilute Li insertion/extraction voltage window would require passivation of the electrode-electrolyte interfaces causing capacity fade and/or incurring additional material processing cost. Therefore, not only the band gap but also the dilute Li insertion/extraction voltages are important to estimate the thermodynamic potential window that the LGPS material is stable (non-reacting) as an electrolyte.

From the above discussion on the unknown facts about LGPS, we attempt to address the following issues from density functional theory calculations:
- The dimensionality of Li-diffusion in LGPS
- Whether there is any distinction between 'structural' and 'diffusive' Li ions in LGPS structure

- How Li-diffusivity is related to the changes in Li concentration and Ge/P ordering
- The thermodynamically reversible potential window for LGPS as well as for the family of the solid electrolytes having similar stoichiometry as LGPS

2. Methodology:

We use density functional theory (DFT) as implemented in VASP (Vienna Ab-initio Simulation Package)[7, 8] to calculate the $T = 0K$ total energies for bulk solids. We use Projector Augmented Wave (PAW)[9] pseudo-potentials corresponding to Generalized Gradient Approximation (GGA)[10] as outlined by Perdew, Burke and Ernzerholf (PBE)[11]. After a systematic convergence test, we choose a $4{\times}4{\times}3$ Γ–centered *k*-point grid in the primitive unit cell of LGPS structure for the energy minimization calculations, relevant for the pre-MD relaxation and the dilute voltage estimation. For the energy minimization calculations, we choose the cut off energies for the plane wave basis set to be 380 eV, 380 eV and 520 eV for the sulphide, selenide and the oxides compounds, respectively. For diffusivity calculations, we use Ab-initio MD simulation under the framework of VASP. For the MD simulations, we use a minimal Γ–centered $1{\times}1{\times}1$ *k*-point grid. After the structural relaxation at 0 K, LGPS is assigned a low temperature (100 K) according to the Boltzman distribution at the start of the MD simulation. The temperature is then ramped up to the desired high temperature in 2 ps at 1 fs timestep to reduce the instability associated with the high temperature MD simulation. At the desired temperature, the material is equilibrated for 5 ps and then the diffusivity data collection occurs for 300 ps at 1 fs timestep. We run MD simulations at high temperature (at 600 K, 800 K, 1000 K, 1200 K, 1400 K and 1600 K) to speed up the diffusivity in order to minimize the computation time. The extrapolation of the high temperature diffusivities is obtained using the Arrhenius relation.

3. Results and Discussions

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3.1 Abbreviations and AcronymsDirectionality of Li-diffusion in $Li_{10}GeP_2S_{12}$

The calculated Li diffusivity in $Li_{10}GeP_2S_{12}$ as a function of temperature is plotted in figure 1. The high temperature diffusivity values are extrapolated to room temperature as shown by the Arhenius line in figure 1. The calculated room temperature diffusivity is $5.55{\times}10^{-8}$ cm^2/s, which results in ionic conductivity of 7.23 mS/cm. The calculated activation barrier to be 240 meV. The room temperature conductivity and activation barrier values are remarkably close to the experimentally measured values (12 mS/cm and 240 meV, respectively) [1] and similar to previously calculated values (9 mS/cm and 210 meV respectively) [2].
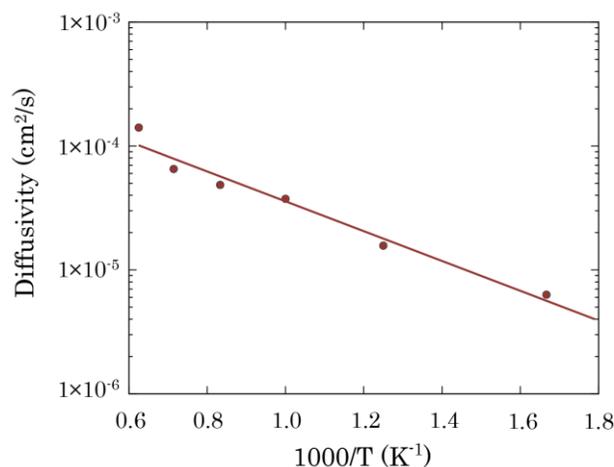
Fig 1. Arhenius plot of Li diffusivity as function of absolute temperature: The dots represent the calculated diffusivities and the line is the fitted straight line that represents the extrapolation curve.

About the diffusion mechanism in the LGPS structure, the original experimental study[1] concluded from the anisotropic thermal vibrational ellipsoids that all the diffusion occurs through the 1D channels along the *c*-direction. One of the previous computational studies, however, have found this material to be a 3D diffuser, though the *ab* plane diffusivity is significantly smaller than that in the *c*-direction[2]. This study found room temperature conductivities to be 40 mS/cm and 0.9 mS/cm (in *c*-direction and *ab*-plane, respectively) and activation barriers to be 170 meV and 280 meV (in the same order). Adams et al. studied LGPS using classical potential MD and found similar activation barriers (190 meV and 300 meV in *c*-direction and *ab*-plane respectively)[12]. However, they found that the diffusion is almost isotropic above 450 K.
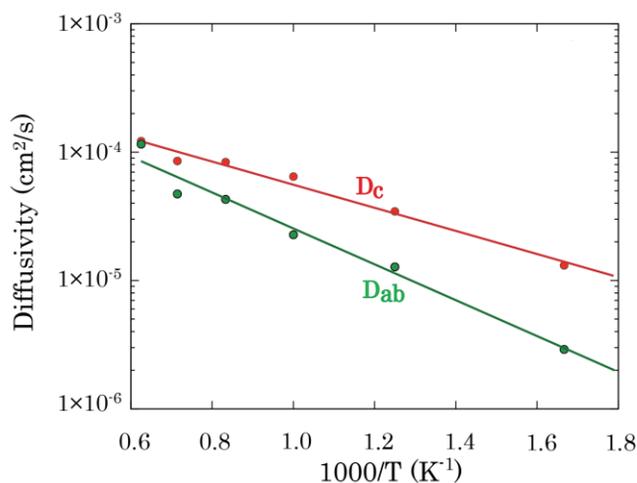

Fig 2. Arhenius plot of the directional Li diffusivity as a function of absolute temperature: The dots represent the calculated diffusivities and the lines are the fitted straight lines that represent the extrapolation curves. Diffusivity in *c*-direction is represented by the top red line and diffusivity in the *ab*-plane is represented by the bottom green line.

We calculate the directional diffusivities as functions of temperature to understand which one of the above three pictures (1D diffusion, highly anistropic but 3D diffusion, anisotropic 3D diffusion at room temperature which becomes isotropic above 450 K) is the most accurate. The Arrhenius plot for the directional diffusivities is shown in figure 2. We find that the diffusion is predominantly in *c*-direction (room temperature conductivity is 59 mS/cm and activation barrier is 180 meV), however there occurs significant diffusion in the *ab*-plane as well (room temperature conductivity is 2 mS/cm and activation

barrier is 280 meV), which possibly helps LGPS to sustain high Li-conductivity after repeated cycling as a pure 1D conductor would soon lose conductivity because of the blocked channels due to antisite defects. We find no data to support that above 450 K, diffusion becomes isotropic. From our calculations, the diffusion becomes isotropic at really high temperature (~1600 K).

3.2   Are there any non-diffusiong "structural" lithium?

In the experimental investigation on LGPS superionic conductor[1], it is reported that among three types of Li sites (16h, 8f and 4d), Li ions from only two types of sites (16h and 8f) participate in diffusion and 4d Li-sites contain non-diffusing or structural Li-ions. The conclusion about the structural Li-ions is based on the construction of thermal ellipsoids around the atom positions. The computational studies on this material did not report existence of two types of Li-ions in the structure (diffusing and structural)[2, 13].

We explicitly compared the diffusivities of two types of Li-ions and find that the 'structural' Li-ions (at 4d sites) are just as diffusive as the 'diffusive' ones (at 16h and 8f sites). At 1000 K, calculated diffusivities are 3.9×10^{-5} cm^2/s and 3.0×10^{-5} cm^2/s for the diffusing and structural Li-ions, respectively. In c-direction, diffusivities are 7.5×10^{-5} cm^2/s and 8.48×10^{-5} cm^2/s for the diffusing and structural Li-ions, respectively, at 1000 K. However, in ab-plane, structural Li's are certainly less diffusive (3.1×10^{-6} cm^2/s at 1000 K) compared to the diffusing Li's (2.1×10^{-5} cm^2/s at 1000 K). The calculated diffusivities clearly show that the so called 'non-diffusing' or 'structural' Li ions are slightly slower in the ab-plane diffusion but as fast in the c-direction (which is the predominant direction of diffusion) as other Li-ions in the LGPS structure.

3.3   Effect of Li-concentration and Ge-P ordering on Li-diffusivity

In the LGPS structure, there are 28 lithium interstitial sites in the primitive cell (consisting of two formula units of Li$_{10}$GeP$_2$S$_{12}$) of which only 20 sites are occupied by Li.[1] Among three types of lithium sites (16h, 4d and 8f), the 4d sites are fully occupied by Li (which erroneously led to the idea of considering these Li-ions to be non-diffusing, as discussed in the last subsection)[1]. The other two types of interstitial sites (16h and 8f, 24 in total) are partially occupied. There are two types (4d and 2b) of Ge/P sites as well. The 2b sites are fully occupied by P atoms in the L$_{10}$GeP$_2$S$_{12}$ structure while 4d sites are half-filled by Ge atoms. Though Ge/P sites are fully occupied in Li$_{10}$GeP$_2$S$_{12}$ structure, variation in the numbers of Li atoms in the structure can potentially lead to change in the relative occupancy of Ge and P atoms to maintain charge balance. The partial occupancy in the Li sublattice and variable occupancy in the Ge/P sublattice are intriguing as they allow for nucleation of the off-stoichiometric compounds which can be relevant as Li-ions diffuse through the material during cycling.
In the primitive cell (consisting of two formula units of L$_{10}$GeP$_2$S$_{12}$), there are 6 Ge/P sites. We consider a four formula unit supercell where there are 12 Ge/P sites and 56 Li sites. The variation of the relative number of Ge and P atoms can accommodate variable number of Li atoms while maintaining charge neutrality: two extreme compositions would be (a) 36 Li when all the 12 Ge/P sites are occupied by P and (b) 48 Li when all the Ge/P sites are occupied by Ge. The compositions in between these two extreme compositions consist of different Ge/P ratio and partially occupied Li sublattice. The search for the ground state structures for these compositions is a huge combinatorial problem itself because it involves two interdependent sublattices. Here, we used electrostatic ground state searching for the Ge-P ordering for random choice of Li-vacancy ordering. During diffusion, Li-vacancy ordering changes continually, hence a choice of random Li-vacancy ordering. We relaxed five different Ge-P orderings having lowest electrostatic energies with DFT for each Li-concentration before performing ab-initio MD simulation. The variation in the Ge-P ordering and Li-concentrations allow us to explore the variability of Li-diffusivity with both these factors which we show in figure 3.
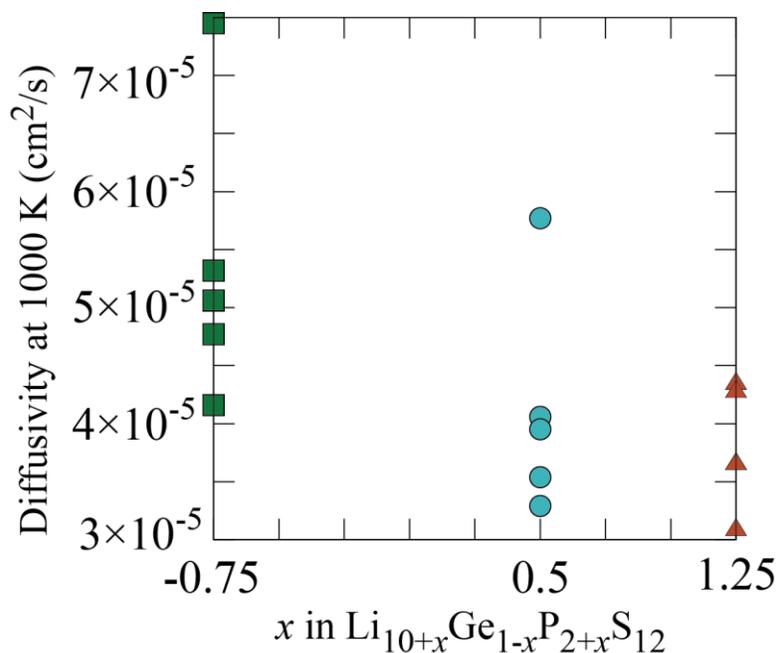
Figure 3. Comparison of calculated diffusivities with a change in Li-concentration and a change in Ge-P arrangement: the abscissa represents the Li concentrations and the data points in same legend along a vertical line represent different Ge-P arrangements in a single Li-concentration. We note that the variation of diffusivity with both the Li-concentration and the Ge-P arrangements are small (a factor of 2).

We choose three Li-concentrations around the stoichiometric compound $Li_{10}GeP_2S_{12}$. We note that with increasing Li concentration, there is a decrease in the Li-diffusivity. However, this variation is small compared to the variability with the change in Ge-P ordering. The kinetics of the change in Ge-P ordering at a particular Li-concentration is beyond the scope of this study. However, we note that even if the kinetics of change between different Ge-P ordering is fast enough, it alters Li-diffusivity by a factor of ~2 only. The variability of Li-diffusivity with concentration is even smaller.

3.4   Dilute Li insertion/extraction voltage for Li10GeP2S12 and related materials and the effect on cell thermodynamics

In order to understand the effect of variable concentration of Li in the electrolyte and the cell thermodynamics, we have calculated the voltages for inserting and extracting dilute Li in LGPS type materials.

Along with the superionic conductor, LGPS, we have considered several iso-structural materials having the ions from the neighbourhood in the periodic table (Al, Si, Ga along with Ge, As along with P and O and Se along with S). Among these ions, Si-Ge, As-P and O-S-Se ions are isovalent. Al and Ga are aliovalent to Ge, though. We appropriately alter the number of Li atoms to accommodate the change in valence of the cations in the structure.

In the primitive cell of LGPS, we systematically introduced Li-vacancy in 20 Li sites one at a time to find the most favourable site to extract the first Li. Similarly, there are 8 vacant sites of in the Li-sublattice which were filled by Li one at a time to find the most favourable site to insert one extra Li.

The same procedure is followed for all other compounds. The dilute voltages are calculated with reference to the Li-metal anode.

The calculated voltages for dilute Li insertion and extraction are reported in table 1. For the LGPS material, for example, the calculated dilute voltages are 0.78 V and 2.97 V for insertion and extraction of Li, respectively. The physical implication of these dilute voltages would be the following: when the cell potential drops below 0.78 V, LGPS electrolyte consumes an extra Li (per primitive cell) and when the cell potential rises above 2.97 V, LGPS electrolyte loses its first Li. The source or sink of Li atoms in a Li-ion battery are typically the electrodes. However if the cell containing LGPS electrolyte is operated beyond the window of dilute voltages (0.78 – 2.97 V), the electrolyte acts as a source or sink for the Li-ions as well. If the dilute voltages for the electrolyte lie between the operating voltages of a cell (a Li-ion operates typically in the range of 0-4 V), the energy density is affected by the side reactions at the electrode-electrolyte interface. Previously, Osaki et al. found that LGPS starts to react with the bulk Li-metal anode when the potential drops below 0.8 V which is remarkably close to what we find from the dilute Li-insertion voltage (0.78 V).[12]

The dilute voltages provide a conservative estimate of thermodynamic stability range for the electrolyte. Nonetheless, a passivation layer between the electrolyte and the electrodes can prevent the side reactions (by not allowing electrons to reach the electrolyte) similar to the SEI (Solid Electrolyte Interface) layer formed in case of liquid electrolytes. Use of some coating material or formation of such layer during first few cycles can allow the electrolytes to work beyond the thermodynamic stability window.

Till date, there are very few experimental studies on the LGPS solid electrolyte that involves electrochemical cycling in a cell. The original experimental report [1] showed data for only 8 cycles and a later report [13] showed only the first cycle voltage-capacity curve at different current. The consumption of electrolyte in irreversible side reactions with the electrode would have a cumulative effect which will incapacitate the cell over repeated cycling. We believe that the evidence of 0-6 V potential window of LGPS electrolyte, shown by Hassoun et al.,[14] would be a result of formation of some passivation layer at the electrode-electrolyte interface, which need to be explored with further experiments. On the other hand, Yamada et al.[15] found evidence that LATP type solid electrolyte got depleted of the Li-ions near the cathode interface at high potential which we believe to be related to the operation outside the voltage window for the electrolyte.

The dilute voltages provide information about the potentials for which the electrolyte would initiate consuming/loosing Li-ions. However, they do not provide information about the range of Li-consumption with the change in cell potential. To know the relationship between cell potential and Li-concentration in the solid electrolyte, one would need to perform more detailed calculations to construct free energy diagram as a function of Li-concentration, which we do not attempt here. Therefore, from the dilute voltages listed in table 1, it is not possible to quantify the loss of capacity of the cell.

Table 1. Calculated voltages for dilute Li insertion and extraction for the compounds having similar stoichiometry and structure as $Li_{10}GeP_2S_{12}$: The neighbourhood of Ge (Al, Ga and Si), P (As) and S (O and Se) in the periodic table is explored to explore possible compounds with similar stoichiometry. The Li content is altered to maintain charge neutrality for the compounds where the valences of the cations are not identical with the valences of the cations in LGPS.

	Compound	Dilute Li insertion voltage (V)	Dilute Li extraction voltage (V)
Sulphide	$Li_{11}AlAs_2S_{12}$	2.15	2.15
	$Li_{11}AlP_2S_{12}$	0.79	2.17
	$Li_{11}GaAs_2S_{12}$	1.83	2.35
	$Li_{11}GaP_2S_{12}$	1.31	2.70
	$Li_{10}GeAs_2S_{12}$	1.71	2.94
	$Li_{10}GeP_2S_{12}$	**0.78**	**2.97**
	$Li_{10}SiAs_2S_{12}$	1.05	2.83
	$Li_{10}SiP_2S_{12}$	0.83	2.77
Selenide	$Li_{11}AlAs_2Se_{12}$	1.73	2.53
	$Li_{11}AlP_2Se_{12}$	0.75	2.33
	$Li_{11}GaAs_2Se_{12}$	1.74	2.55
	$Li_{11}GaP_2Se_{12}$	0.78	2.34
	$Li_{10}GeAs_2Se_{12}$	1.78	2.66
	$Li_{10}GeP_2Se_{12}$	1.21	2.59
	$Li_{10}SiAs_2Se_{12}$	1.34	2.63
	$Li_{10}SiP_2Se_{12}$	1.18	2.49
Oxide	$Li_{11}AlAs_2O_{12}$	2.31	2.28
	$Li_{11}AlP_2O_{12}$	-1.00	3.75
	$Li_{11}GaAs_2O_{12}$	2.50	1.73
	$Li_{11}GaP_2O_{12}$	-0.26	3.22
	$Li_{10}GeAs_2O_{12}$	0.38	4.72
	$Li_{10}GeP_2O_{12}$	-0.70	4.45
	$Li_{10}SiAs_2O_{12}$	0.38	4.16
	$Li_{10}SiP_2O_{12}$	-1.29	4.35

For an ideal solid electrolyte for a typical Li-ion cell, the dilute voltages should be negative (for insertion) and > 4 V (for extraction) so that in the range of operating potential, solid electrolyte does not participate in the lithium exchange process other than transporting Li as a non-reacting diffuser. In figure 4, we show the same dilute voltages that are reported in table 1 in a different form. We choose the boundaries for the preferred zone in a less conservative manner: 0.5-3.5 V instead of 0.0-4.0 V. In figure 4, the lower right corner is the preferred zone of dilute voltages. We note that all the compounds in this zone are oxides. In a previous computational study [5], similar compounds have been studied for their thermodynamic stability and it was concluded that the oxides are most unstable compared to the sulphides and the selenides. Therefore, it is possible that all the preferred solid electrolytes we find in this study may be unstable and impossible to synthesize at the first place.

In figure 4, we further note that all the sulphide and selenide compounds, that are isostructural with LGPS, fall in the upper left corner of the plot, the most undesirable zone. The LGPS electrolyte is highlighted with purple color. The red dots in figure 4 correspond to $Li_{11}AlAs_2O_{12}$ and $Li_{11}GaAs_2O_{12}$,

which have a lower Li-extraction voltage than Li-insertion voltage, which indicates that the compositions are not on the convex hull along the axis of Li-concentration variation and hence unstable.
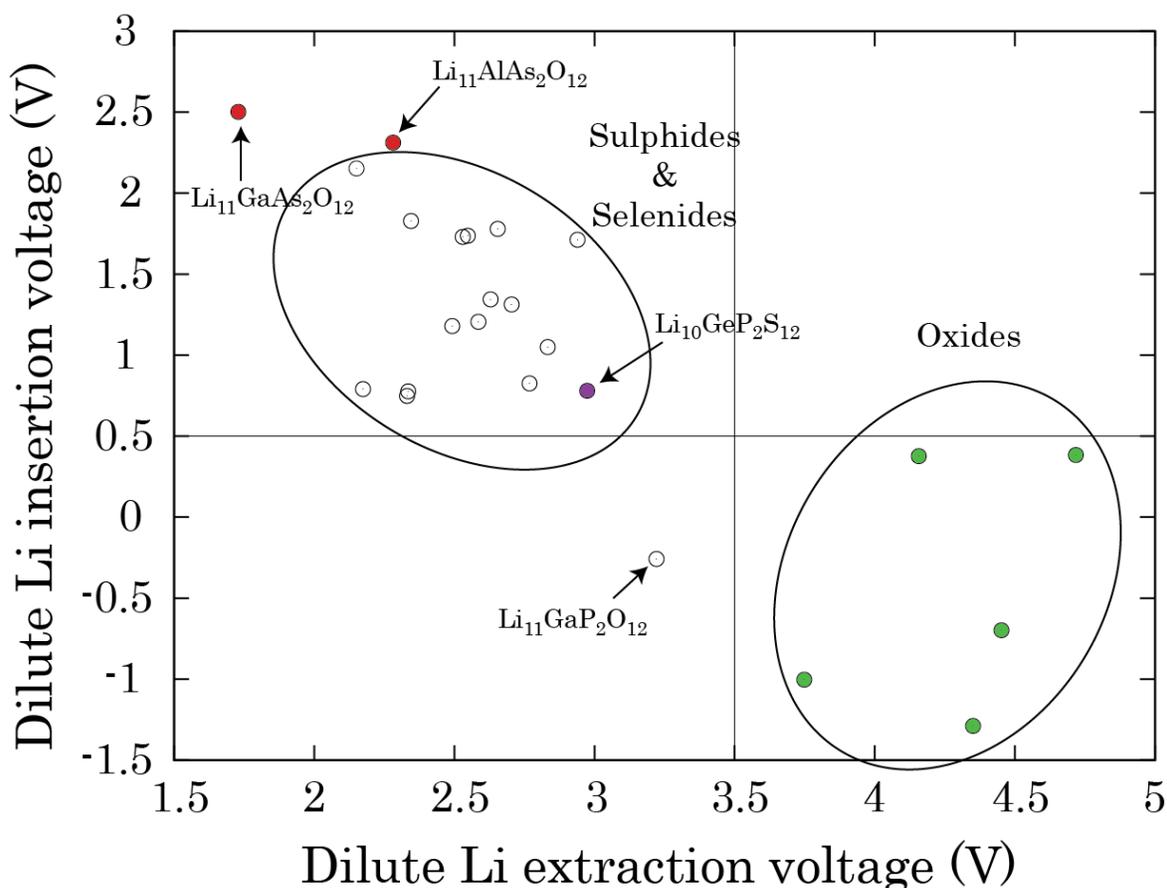

Fig 4. Calculated dilute Li insertion and extraction voltages for the family of $Li_{10}GeP_2S_{12}$: content in table 1 is pictorially shown in this figure to emphasize the trend. LGPS is highlighted with purple color. The red dots correspond to $Li_{11}MAs_2O_{12}$ (M = Ga/Al), for which the dilute Li-insertion voltage is lower than dilute Li-extraction voltage indicating an unphysical situation of non-convex hull with respect to Li-concentration suggesting that these compounds are not stable.

Though thermodynamics of cell-cycling is affected by Li insertion/extraction to/from the solid electrolyte, we do not envision any significant change in cell kinetics as Li-transport behaviour of the electrolyte is not a strong function of Li-concentration, as shown in figure 3.

4. Conclusions:

We attempt to address few unanswered questions about the LGPS solid electrolyte in this study. We find that Li diffusivity is predominant in *c*-direction and it is significant enough in the *ab*-plane. All the lithium ions in the LGPS structure (in different Wyckoff sites) are equally mobile and there is no 'structural' Li. The variation of Li-diffusivity is not very significant with changes in Li-concentration or local Ge-P orderings. We calculate the dilute Li-extraction/insertion voltages for the family of LGPS-type materials and find the thermodynamic limit of these electrolytes to be small which would require some passivation between the electrode and electrolyte for long cycle life of the electrolyte. With respect to the thermodynamic limit of cell-potential, oxides are the most attractive compared to the sulphides and selenides.

5. Acknowledgment:

6. References:

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