"Superionic Diffusion through Frustrated Energy Landscape"

Di Stefano, Davide; Miglio, Anna; Robeyns, Koen; Filinchuk, Yaroslav; Lechartier, Marine; Senyshyn, Anatoliy; Ishida, Hiroyuki; Spannenberger, Stefan; Prutsch, Denise; Lunghammer, Sarah; Rettenwander, Daniel; Wilkening, Martin; Roling, Bernhard; Kato, Yuki; Hautier, Geoffroy

ABSTRACT

Solid-state materials with high ionic conduction are necessary for many technologies, including all-solid-state lithium (Li)-ion batteries. Understanding how crystal structure dictates ionic diffusion is at the root of the development of fast ionic conductors. Here, we show that LiTi2(PS4)3 exhibits a Li-ion diffusion coefficient about an order of magnitude higher than that of current state-of-the-art Li superionic conductors. We rationalize this observation by the unusual crystal structure of LiTi2(PS4)3, which offers no regular tetrahedral or octahedral sites for Li to favorably occupy. This creates a smooth, frustrated energy landscape resembling the energy landscapes present in liquids more than those in typical solids. This frustrated energy landscape leads to a high diffusion coefficient, combining low activation energy with a high pre-factor.

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LiTi₂(PS₄)₃ exhibits a Li diffusion coefficient about an order of magnitude higher than that of state-of-the-art superionic conductors, such as Li₁₀GeP₂S₁₂. This is rationalized by the unusual LiTi₂(PS₄)₃ crystal structure, which offers no regular tetrahedral or octahedral sites for Li to favorably occupy. This creates a smooth Li-anion interaction energy landscape favoring not only low energy barriers but also a higher pre-factor for the diffusion coefficient. The higher pre-factor is linked to longer jump distances and higher entropy for the transition state.
Superionic Diffusion through Frustrated Energy Landscape

Davide Di Stefano, Anna Miglio, Koen Robeyns, Yaroslav Filinchuk, Marine Lechartier, Anatoliy Senyshyn, Hiroyuki Ishida, Stefan Spannenberger, Denise Prutsch, Martin Wilkening, Yuki Kato, and Geoffroy Hautier

SUMMARY

Solid-state materials with high ionic conduction are necessary for many technologies, including all-solid-state lithium (Li)-ion batteries. Understanding how crystal structure dictates ionic diffusion is at the root of the development of fast ionic conductors. Here, we show that LiTi$_2$(PS$_4$)$_3$ exhibits a Li-ion diffusion coefficient about an order of magnitude higher than that of current state-of-the-art Li superionic conductors. We rationalize this observation by the unusual crystal structure of LiTi$_2$(PS$_4$)$_3$, which offers no regular tetrahedral or octahedral sites for Li to favorably occupy. This creates a smooth, frustrated energy landscape resembling the energy landscapes present in liquids more than those in typical solids. This frustrated energy landscape leads to a high diffusion coefficient, combining low activation energy with a high pre-factor.

INTRODUCTION

Understanding and controlling ionic conduction in solids are driving the development of many devices from sensors to fuel cells. In the field of lithium (Li)-ion or sodium (Na)-ion batteries, ionic transport in the electrode and electrolyte is often a bottleneck to higher rates and power. The development of superionic conductors for solid-state electrolytes has been a recent focus. All-solid-state batteries would offer opportunities in terms of better power, energy density, and stability than those of Li-ion battery technologies based on organic liquid electrolytes. In addition, solid-state electrolytes could facilitate the development of next-generation batteries, such as Li-S or Li-O$_2$ batteries. However, very high ionic diffusion or conductivity in solids (i.e., comparable or close to that of liquids) at room temperature is an unusual phenomenon. Only a handful of crystalline-structure families—such as beta-alumina, NASICON, garnet, argyrodite, and Li$_{10}$GeP$_2$S$_{12}$ (LGPS)—have been reported as alkaline superionic conductors.

In the case of Li conductors, the Li ionic conductivity ($\sigma$) depends on the Li conductivity (or charge) diffusion coefficient ($D_\sigma$) and the concentration of mobile Li ($n_{Li}$) through $\sigma = n_{Li}D_\sigma q^2 kT$, where $q$ is the charge of the diffusing species, $k$ is the Boltzmann constant, and $T$ is the temperature. $D_\sigma$ is indicative of how easily Li ions collectively flow when an electric field is applied. It is formally related to the tracer Li diffusion ($D_t$) coefficient by a factor called the Haven ratio: $D_\sigma = D_t H$. The Haven ratio for a typical ionic conductor usually ranges from 0.1 to 1, whereas the tracer diffusion can vary by orders of magnitude between different materials. The tracer diffusion typically follows an Arrhenius law where $D_t = D_{0t}e^{-\frac{E_a}{kT}}$. The activation energy ($E_a$) can be directly linked to the energy barriers necessary to jump between...
crystalline sites. Factors leading to superionic conductivity\textsuperscript{10} include diffusion volumes and bond-valence paths,\textsuperscript{11} phonon frequencies,\textsuperscript{12} face-sharing tetrahedral networks,\textsuperscript{13} or correlated cationic movements.\textsuperscript{14} Since the beginning of the study of superionic conductors, the idea of developing solids with a frustrated energy landscape (i.e., for which no specific configuration for the mobile ions is favored) has been discussed because it would lead to a diffusion behavior similar to that in liquids. In this regard, different types of frustration mechanisms have been recently put forward to explain high diffusion in garnets,\textsuperscript{15} argorydite,\textsuperscript{16} nanostructured Ba\textsubscript{1-x}Ca\textsubscript{x}F\textsubscript{2},\textsuperscript{17} multivalent cation electrodes,\textsuperscript{18} and borohydrides.\textsuperscript{19,20}

Here, we show that LiTi\textsubscript{2}(PS\textsubscript{4})\textsubscript{3} (LTPS) exhibits a very high Li-ion diffusion coefficient. The origin of the very fast diffusion is elucidated by a detailed analysis of the frustrated energy landscape in this material.

**RESULTS**

We prepared samples of LTPS by using a solid-state reaction (see Supplemental Information section “Synthesis” and Figure S1). Powder X-ray diffraction (PXRD) measurements confirmed the purity of the previously identified LTPS phase (Figure S2).\textsuperscript{21–23} We evaluated the Li tracer diffusion coefficient in LTPS by using \textsuperscript{7}Li pulsed field gradient (PFG) nuclear magnetic resonance (NMR) at several temperatures (Figure S3 and Table S1). Figure 1 compares the measured Li diffusion coefficient versus temperature between LTPS (in red) and known solid (in blue) and liquid (in black) electrolytes.\textsuperscript{24–28} A difference of more than one order of magnitude exists between liquid electrolytes and state-of-the-art solid-state electrolytes. This diffusion “gap” is partially filled by LTPS. At room temperature, LTPS exhibits a tracer diffusion coefficient that is significantly higher (around $1.2 \times 10^{-11}$ m$^2$/s) than that of the best solid Li conductors from the LGPS family. Its activation energy is around 246 meV and similar to that of LGPS (220 meV). The pre-factor ($D_0$) of 2.94 $\times$ 10$^{-7}$ m$^2$/s of LTPS is about 20 times higher than that of LGPS (1.31 $\times$ 10$^{-8}$ m$^2$/s). We probed the conductivity of LTPS by using impedance spectroscopy on pressed powder samples and found a Li grain ionic conductivity of 6.1 mS/cm at 300 K (Figures S4 and S5). We estimated an electronic conductivity of $8.2 \times 10^{-8}$ S/cm from direct current (DC) polarization by using an ion-blocking cell (Figure S6). The activation energy of 277 meV extracted from impedance data...
is in agreement with the PFG-NMR data. Using the measured ionic conductivity and tracer diffusion, we evaluated an experimental Haven ratio at around 0.24, on par with that of other solid-state electrolytes, such as LGPS.

The grain conductivity of LTPS is already competitive with that of the best solid-state electrolytes, such as LGPS (12 mS/cm).\(^8\) The lower Li concentration in LTPS than in LGPS is compensated by its higher diffusion coefficient. The main factor limiting the direct use of LTPS as a solid-state electrolyte is the presence of Ti\(^{4+}\), which is redox active in the voltage window of interest for Li-ion batteries. We note that computational results on the LTPS crystal structure, where Ti was substituted with Zr (a non-redox active element), showed very similar diffusion. This points to a diffusion mechanism strongly linked to the LTPS crystal structure (Figure S7).

We performed extensive structural characterization to understand the crystal chemistry of LTPS by using a combination of X-ray synchrotron and neutron powder diffraction, as well as X-ray diffraction on a single crystal (Tables S2–S4). Kim et al. reported a \(P\bar{6}\)cc space group for LTPS.\(^{22,23}\) However, we found an orthorhombic \(C\bar{c}c_2\) structure (Figure S2), which is a superstructure of \(P\bar{6}\)cc. These structures are very close to each other. The orthorhombic \(C\bar{c}c_2\) structure exhibits slightly lowered 3-fold point symmetry from hexagonal \(P\bar{6}\)cc. The structure presented in Figures 2A and 2B shows TiS\(_6\) octahedra connected by edge-sharing thiophosphate (PS\(_4\)) groups (Figure S8). Through \(^{31}\)P magic angle spinning (MAS) NMR, we were able to resolve almost all magnetically distinct phosphorous sites in crystalline LTPS with chemical shifts smaller than 80 ppm (see Figure S9). Narrow lines point to a well crystalline sample; the broad signals typically seen for thiophosphate glasses are absent. Therefore, we conclude that the crystalline structure of LTPS causes the high Li diffusivity probed by PFG NMR rather than any amorphous side phase, whose amount seems to be negligible. Single-crystal synchrotron X-ray diffraction experiments revealed Li ordering at 150 K (Table S3) and melting of the Li-ion substructure at higher temperatures. In particular, Li positions cannot be localized on the same crystal at room temperature, which is an indication of high Li mobility.
To gain further insight in the atomistic mechanisms controlling diffusion, we used *ab initio* molecular dynamics (AIMD) simulation within density functional theory (DFT). Experimentally, the unveiled space group \( \text{Ccc}2 \) for Li\(_2\)(PS\(_4\))\(_3\) was also independently obtained during a DFT optimization of the \( \text{P}6\text{cc} \) initial model (see “Structural Characterization” in the Supplemental Information), and the computed crystal structure was very close to the experimental one (Figure S10). From the AIMD simulation, the tracer diffusion could be extracted after the root-mean-square displacement of the Li atoms with time (see Supplemental Information). The AIMD simulation provided an activation energy of 197 meV, in fair agreement with experimental data (Figures S11 and S12). The Haven ratio can also be estimated with AIMD data, and we found a Haven ratio of 0.3, in good agreement with experimental data. The higher pre-factor in LTPS than in other superionic conductors, such as LGPS, was reproduced by our computational results (Figure S13). Although not constrained by symmetry, diffusion in LTPS was computed to be almost isotropic (Figure S12). Figure 2C shows an in-plane view of the LTPS crystal structure, where Li-ion probability density was obtained from the AIMD simulation at the temperatures 1,200 and 600 K (more temperatures are provided in Figure S14). We can access the Li diffusion paths by using these probability density plots. It is noticeable that the large pore present in LTPS does not accommodate any Li diffusion. Instead, Li diffuses closely according to the Ti-P-S framework, forming “rings” around the Ti sites in the \( a-b \) plane. In Figure S15, a tilted view of the structure indicates that those rings are also connected in the \( c \) direction, leading to a 3D diffusion network. The lower-temperature data (600 K; Figure 2C) show the appearance of Li “pockets” of high Li probability. Three of these pockets constitute one “ring.” The Li ions jump between the pockets either within the ring (intra-ring jumps; blue arrows) or between rings (inter-ring jumps; red arrows). We observed from the molecular dynamic simulations that the fastest, higher-rate jumps were intra-ring and that the inter-ring jumps happened at a lower rate. The inter-rings jumps were the limiting steps for Li macroscopic diffusion. Experimental complementary insight on this microscopic mechanism was also provided by \(^7\text{Li-NMR} \) relaxometry experiments (Figure S16), which identified two jumps that we related to the inter-ring and intra-ring processes. The inter-ring jump rate extracted from NMR relaxometry is in good agreement with our PFG-NMR diffusion coefficient.

We observed that the pockets of high Li probability were not typical crystallographic sites (e.g., octahedral or tetrahedral) and were much larger “potato”-shaped regions, even at room temperature (obtained from AIMD at 300 K; see Figures 2D and S17). This is unusual given that alkali diffusion mechanisms in crystalline superionic conductors are typically described by jumps between connected crystallographic sites: tetrahedral-tetrahedral sharing faces, for instance, in the LGPS family or tetrahedral-octahedral-tetrahedral faces for garnets.\(^{13}\) Observation of the Li-S coordination number for LTPS in these pockets shows that Li experiences an average coordination between 3 and 4, far from the typical regular tetrahedral sites occupied, for instance, in LGPS (Figure S18). This low coordination is rare given that Li sits in quite regular tetrahedral or octahedral sites in the vast majority of sulfides (Figure S19). We link the unusual and energetically unfavorable coordination in LTPS and the occupation of large pockets to the absence of any regular tetrahedral (or octahedral) site in the Ti-P-S crystalline framework in which Li could favorably sit. To test this hypothesis, we performed a local environment analysis of all (occupied by Li and unoccupied) sites in LTPS to demonstrate the absence of undistorted tetrahedral sites favorable to Li (Figure S20). Figure 3A shows, in dashed black, a measure of the distortion of occupied Li tetrahedral environments in sulfide compounds from the stable materials listed in the Materials Project database (Figures S20 and S21).\(^{24,29}\) This analysis provides a range of the typical distortions that are acceptable...
Figure 3. Li-Site Distortion and Diffusion Mechanism in LTPS

(A) In dashed black is the distribution of tetrahedral-site distortion (tetrahedricity) for the sites occupied by Li in stable sulfides contained in the Materials Project database. In red and blue is the distribution of tetrahedral-site distortion for all (both occupied by Li and unoccupied) sites in LTPS and LGPS. The tetrahedra at the top indicate how tetrahedricity measures the distortion of the tetrahedron.
for a tetrahedral site to favorably accept Li in sulfides. The red curve in Figure 3A shows the distribution of distortion for all tetrahedral sites in LTPS. The distribution of LTPS sites indicates that all available sites are highly distorted, providing no favorable sites for Li to occupy. For comparison, the distribution of all available sites in LGPS is drawn in blue, indicating a distribution range close to that of sulfides present in the Materials Project. An analysis on octahedral sites leads to a similar conclusion (Figure S22).

The crystalline Ti-P-S framework provides only very distorted tetrahedra for Li to occupy. Given that distorted tetrahedral sites are less energetically favorable for Li (Figures S23 and S24), the Li experiences in LTPS a frustrated energy landscape (i.e., for which no specific configuration for the mobile ions is favored). Additional evidence from sampling the LTPS framework with different configurations of Li by using DFT also indicates that the energy landscape felt by Li is smooth and frustrated (Figure S25). This frustration mainly comes from the Ti-P-S framework and not from Li-Li interactions, as indicated by the lack of dependence of the site energy distribution and the tracer diffusion on changes in Li content (Figure S26). This is different than the frustration described in other ionic conductors, such as garnets.15

In a simple model, two main interactions can be used for understanding the energy landscape of Li in an ionic conductor: a short-range Li-anion interaction and a longer-range electrostatic Li-cation (P5+ and Ti4+ in LTPS) interaction. The two components (Li-anion and Li-cation) are schematically described for a 1D model of a traditional alkaline superionic conductor in Figure 3B. The Li-anion interaction is modulated by the alternation of stable Li sites separated by energy barriers because Li needs to squeeze through a small polyhedral face or edge to reach the next stable site. Li-cation interactions are also present and tend to have a much longer modulation on the order of the distance between cations. In the resulting total energy landscape, the energy barriers and the jump distances for Li diffusion are mainly set by the Li-anion interaction. Li transport in these traditional superionic conductors, such as LGPS, can be understood by a model considering Li in an anion lattice (bcc, fcc, or hcp) and a diffusion mechanism through small jumps of around 2Å between tetrahedral or octahedral sites, as demonstrated, for instance, by Ceder and co-workers.13 On the other hand, in the case of LTPS, Li occupies much larger potato-shaped pockets composed of several (highly distorted) tetrahedral sites (see Figures 2D and S17). This is the signature whereby the Li-anion interaction does not force Li to occupy the tetrahedral sites and is much smoother for LTPS than for traditional superionic conductors (Figure 3C). The smoothening of the Li-anion interaction naturally increases the weight of the Li-cation interaction in setting the total energy landscape and thus the resulting energy barriers and jump distances. The Li-cation interaction in LTPS is indeed important, in agreement with this simple picture. The Li-cation electrostatic interaction is the lowest in the pocket regions of high Li probability and the strongest at the diffusion bottleneck in the inter-ring region (Figure S27). We note that the energy landscapes in traditional superionic conductors and LTPS differ significantly in their shape and by the importance of the Li-cation interaction (Figures 3B and 3C). The LTPS energy landscape presents broader and softer stable sites separated by longer jump distances.

Figure 3. Continued

(B and C) Li energy landscape for a model 1D system including Li-anion and Li-cation interactions for (B) a typical superionic conductor (e.g., LGPS) and (C) a frustrated-energy-landscape material (LTPS).

(D and E) Differential bond-valence mismatch for Li ([1-bond valence (BV)]) at the transition-state region for LGPS (D) and LTPS (E). For reference, we report the size of the LGPS transition state as a dashed circle on the LTPS figure.
Our result on LTPS shows that when the Li-anion energy landscape is smoothened, the energy barrier related to Li-cation interaction can, in the adequate material, lead to relatively small energy barriers (on par with the best current superionic conductors). The very large difference in the pre-factor of the tracer diffusion measured by PFG NMR between LTPS and LGPS (around a factor 20) remains to be explained. We note that the concerted Li mechanism cannot be responsible for the higher pre-factor. Indeed, the Haven ratio in LTPS was measured to be around 0.24, which is close to that of other superionic conductors, especially LGPS. This indicates that correlated movements are important in LTPS, but not more than in other superionic conductors, such as LGPS. According to transition-state theory, the tracer diffusion coefficient for an interstitial mechanism can be expressed as

$$D_{tr} = \frac{1}{6} a^2 f n_0 z e^{\frac{\Delta S_{mig}}{kT}} D_{E}$$

where $a$ is the jump distance, $f$ is a correlation factor, $n_0$ is the attempt frequency, $z$ is the number of neighbor sites to jump in, $\Delta S_{mig}$ is the entropy of migration, and $\Delta E$ is the energy barrier of migration. The pre-factor is directly influenced by the jump distance ($a$). In contrast to that in traditional superionic conductors, the diffusion in LTPS is not limited to small jumps between polyhedra, and the jump distance can be much longer (Figure 3B versus 3C; Figure S28). We estimate the jump length to be around 6Å in LTPS versus 2Å in LGPS, accounting for a difference of 9 in pre-factor. It is unlikely that the correlation factor ($f$) could account for the remaining difference in pre-factor. The correlation factor cannot be larger than 1, and LGPS is reported to have a correlation factor close to 1.24,25 Additionally, an analysis of the AIMD simulation of LTPS identified only a few inter-ring jumps returning backward (see Supplemental Information). NMR relaxometry provides a direct probe of the jump rate independently of the correlation factor and the jump distance. A comparison between the jump-rate pre-factor $I_0 = n_0 e^{\frac{\Delta S_{mig}}{kT}} D_{E}$ in LGPS (2.5 $\times$ 10^{12} s^{-1})24,25 and LTPS (3.2 $\times$ 10^{12} s^{-1}) extracted from the NMR data shows a higher pre-factor for LTPS (see “7Li NMR Spin-Lattice Relaxation Measurements” in the Supplemental Information), indicating that $I_0$ is also part of the higher tracer diffusion pre-factor in LTPS. Because the stable sites in LTPS are large pockets (Figure 2D), we expect softer vibrational modes than in LGPS, as confirmed by a comparison of the vibrational density of states obtained from the AIMD simulation (see Figure S29). The lower-frequency vibrational Li modes in LTPS lead to a lower attempt frequency ($n_0$) and entropically stabilized stable sites (because softer modes directly lead to higher vibrational entropy). Thus, the larger $I_0$ of LTPS can be accounted for only by a larger entropy of the transition state. Figures 3D and 3E compare the bond-valence mismatch for Li in the transition state for LGPS and LTPS. The region of lower bond-valence mismatch indicates lower energy. LTPS shows a transition state significantly broader than that in LGPS, indicating that it is softer and thus entropically stabilized. This entropical stabilization of the transition state is inherent (as the larger jump length) to the frustrated energy landscape of LTPS because it comes from relaxing the constraint imposed on traditional superionic conductors of having to jump through narrow polyhedral edges or faces.

**DISCUSSION**

LTPS is not the only ionic conductor to present a high pre-factor for its diffusion coefficient. However, a high pre-factor is often correlated with a high energy barrier according to the so-called Meyer-Neldel empirical rule. The combination of a high pre-factor and a low barrier is rare in alkali superionic conductors and only seen in liquid electrolytes (see Figure S30).30 Recently, Zeier and co-workers identified the Meyer-Neldel rule as a serious bottleneck to obtaining high-performance superionic conductors.31 The authors rationalized that the softening of the lattice, which tends to lead to lower energy barriers, is difficult to decouple from a lowering of the
diffusion pre-factor through entropic stabilization of the stable site. Interestingly, LTPS keeps a high pre-factor despite low-frequency soft modes through its long jump distance and entropic stabilization of the transition state. More generally, the high pre-factor, the unusual Li-site behavior (no occupation of a polyhedral sites), and the smoother energy landscape due to frustration are all characteristics of diffusion in liquids. In fact, the analysis of the Li vibrational density of states during AIMD indicates that Li mobility in LTPS resembles a liquid more than that in LGPS (see Figure S29). The reason for the high performance of some previously studied superionic conductors could potentially be rationalized by a frustrated energy landscape similar to that in LTPS. In RbAg4I5, for instance, the mobile Ag+ ions occupy large pockets instead of small polyhedral sites, and the Ag+ ion conductivity is very high at room temperature because of a combination of high pre-factor and low energy barrier.

From its origin, the development of solid ionic conductors has been driven by the ambition to mimic in a solid the diffusion mechanism of a liquid. Most Li superionic conductors (e.g., LGPS and garnets) show ionic-conductivity mechanisms controlled by jumps between crystallographic sites (e.g., tetrahedral and octahedral). Here, we present a superionic conductor LTPS showing a deviation from these localized jumps given that the Li experiences a smooth, frustrated energy landscape. This frustrated energy landscape occurs because the unique crystal structure of LTPS offers no regular polyhedral sites for Li to occupy. This unusual energy landscape influences the diffusion mechanism and leads to a very high Li-ion tracer diffusion as a result of a combination of a low energy barrier and a high pre-factor. This high pre-factor can be directly linked to long jump lengths and high entropy of the transition state. We believe that, although rare, materials exhibiting a frustrated energy landscape are likely to exist in crystal structures other than LTPS. Our work opens the possibility for searching for these exceptional crystalline frameworks through crystal-structure analysis.

EXPERIMENTAL PROCEDURES

Further detailed procedures are described in the Supplemental Information.

Synthesis

Starting materials Li2S, P2S5, and TiS2 were mixed in an appropriate molar ratio in an Ar-filled glovebox. The mixture was put into the ZrO2 pot with a ZrO2 ball (φ 10 mm), and then the mixture was mechanically milled by a planetary ball-milling apparatus at a rotating speed of 370 rpm for 40 h. After the ball-milling procedure, the mixture was put into a quartz tube and heated at 400°C for 8 h to yield powder-state LiTi2(PS4)3. The single crystal was obtained by the heat treatment of ball-milled precursor in a sealed quartz tube at 750°C for 10 h.

Structural Characterization

The crystal structure of LiTi2(PS4)3 was investigated by PXRD, powder-state neutron diffraction, and single-crystal X-ray diffraction measurements. The synchrotron X-ray diffraction was conducted at the BL19B2 beamline at SPRing-8 in Japan. The neutron diffraction data were collected at the high-resolution powder diffractometer SPODI at the FRM-II reactor. In addition to laboratory X-ray diffraction using MoKα radiation generated by a Rigaku UltraX 18S, the single crystals of the title compound were studied at the Swiss-Norwegian Beam Line BM01A at the European Synchrotron Radiation Facility (ESRF; Grenoble, France) with a PILATUS 2M hybrid pixel detector at a wavelength of 0.7149 Å. The structure was characterized on the basis of the
model obtained by single-crystal X-ray diffraction measurements. The structure was also refined by the Rietveld method.

**7Li-PFG-NMR Characterization**

7Li PFG-NMR measurement was performed at 155.6 MHz with an AVANCE III HD spectrometer (Bruker BioSpin). We measured the Li tracer diffusion coefficient at the temperature range of 253–353 K (−20°C to 80°C) by varying the strength of the PFG (g) and its duration (t) from 0 to 25 Tm⁻¹ and 1 to 2.5 ms, respectively.

**Impedance Spectroscopy**

Ionic conductivities were measured by impedance spectroscopy. Powder of LiTi₂(PS₄)₃ was formed into the pellet (φ 6.0 mm) by hot pressing at a temperature of 200°C for 10 min by application of 270 MPa pressure under Ar atmosphere. Ion-blocking Au electrodes were sputtered on both sides of the pellet. The alternating current (AC) impedance was measured in a frequency range from 1 MHz to 0.1 Hz and at temperatures from −130°C to 27°C with a Novocontrol Alpha-AK impedance analyzer.

**7Li NMR Spin-Lattice Relaxation Measurements**

7Li (spin-3/2) spin-lattice relaxation rates in the laboratory frame were recorded with a Bruker 300 AVANCE spectrometer in combination with a static broadband probe (Bruker), which operated at a Larmor frequency of ω₀/2π = 116 MHz. A train of ten 90° pulses (2.5 μs in length) destroyed any longitudinal magnetization in thermal equilibrium; its recovery as a function of waiting time was then recorded until full recovery had been achieved. The magnetization transients were parameterized by stretched exponentials to extract diffusion-induced spin-lattice relaxation rates R₁. The stretching exponents ranged from 1 to 0.8, thus showing only slight deviations from simple exponential recovery. Static 7Li NMR line shapes were recorded after excitation of the spin ensemble with a single 90° pulse; the recycle delay was at least 5 × 1/R₁ to ensure quantitative lines.

**31P NMR Characterization**

31P MAS-NMR measurements were carried out on a Bruker AVANCE 500 MHz spectrometer. The magnetic field of 11.7 T corresponded to a Larmor frequency of 202.4 MHz. We used single-pulse excitation, and the π/2 pulse length was 1.33 μs. We accumulated 16 scans to obtain the spectrum shown here, which was recorded at a spinning frequency of 25 kHz with ambient bearing gas. The recycle delay between each scan was 300 s.

**DFT Computations**

We performed all ab initio computations in this study by using DFT within the Projector Augmented Wave approach as implemented in the Vienna Ab Initio Simulation Package. We used the generalized-gradient approximation from Perdew-Burke-Ernzerhof. The AIMD simulations for LTPS were performed with a time step of 2 fs for a total simulation time of at least 200 ps on an NVT ensemble in an unit cell of 144 atoms with a Γ-centered k-point mesh. We performed all analyses by using pymatgen and the pymatgen-diffusion Python packages.

**DATA AND CODE AVAILABILITY**

All data needed for evaluating the conclusions of this paper are present within the article or the Supplemental Information. The accession numbers for the crystal structure data of LiTi₂(PS₄)₃ reported in this article are CSD: 1940846–1940847.
SUPPLEMENTAL INFORMATION

Supplemental Information can be found online at https://doi.org/10.1016/j.chempr.2019.07.001.

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AUTHOR CONTRIBUTIONS

G.H. and Y.K. designed and managed the project. G.H. and Y.K. wrote the manuscript with help from the other co-authors. D.D.S. and A.M. performed the ab initio computations. D.D.S., A.M., Y.K., B.R., M.W., and G.H. developed the theoretical understanding. D.D.S. performed the local environment and the diffusion mechanism analysis. Y.K. and M.L. synthesized the powder-state and single-crystal LTPS. K.R., Y.F., and A.S. performed the crystal-structure characterization with discussion with Y.K. H.I. measured and analyzed the Li diffusion coefficient of LTPS by working with G.H., Y.K., and M.W. Y.K., S.S., and B.R. measured and analyzed the impedance data. D.P., D.R., and M.W. conducted the $^7$Li NMR relaxometry measurement and analysis. S.L. and M.W. measured and analyzed the $^{31}$P MAS NMR data.

DECLARATION OF INTERESTS

Y.K., A.M., and G.H. are inventors on a patent (PCT/EP2016/076153) assigned to Toyota Motor Europe and related to the presented material.

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