

envisaged. The importance of single-electron chemistry in the synthesis of hypervalent iodine compounds has been demonstrated and is now a viable alternative to the well-established two-electron oxidation with peracids. Despite this exciting success, the search for the “magic oxidant” able to oxidize organic iodines selectively in the presence of any other compounds is still ongoing, given that it would definitively be a major advance in the development of green oxidation methods.

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## Preview

# A Solid with Liquid-like Diffusion: A Unique Superionic Conductor

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**Understanding fast ionic diffusion in solids is key to engineering solid electrolytes for energy storage devices such as all-solid-state batteries. In this issue of Chem, Hautier and co-workers conduct atomistic modeling and nuclear magnetic resonance experiments to illustrate how the unique structure of LiTi<sub>2</sub>(PS<sub>4</sub>)<sub>3</sub> enables unprecedented Li-ion diffusivity.**

Lithium-ion batteries power most portable electronic devices and electric vehicles. Although current commercial lithium-ion batteries use liquid electrolytes, all-solid-state batteries have been increasingly explored thanks to their improved safety and energy density. All-solid-state batteries rely on a solid electrolyte—a solid ceramic or polymer material which has high Li-ion conductivity, chemical stability, and electrochemical stability during voltage cycling.<sup>1,2</sup> However, solids with high Li-ion conductivities comparable to liquid electrolytes, known as superionic conductors, are rare and exhibit highly diverse crystal structures and compositions.<sup>3</sup>

Further, to be used as solid electrolytes, superionic conductors require a number of other properties beyond high Li-ion conductivity, such as good electrochemical stability, mechanical properties, low-cost synthesis and processing, and manufacturability for all-solid-state batteries. The demand for such advanced solid electrolytes has motivated extensive studies on the known superionic conductors to characterize their Li diffusion mechanisms and understand how their crystal structures enable such fast Li-ion diffusion.<sup>4,5</sup>

In solids, ionic diffusion is mediated by ion hopping between inter-connected

sites of ions in the crystal structure of the material. The lower the energy barrier that the ion must overcome to make the hop, the higher rate of hopping, and the faster the diffusion.<sup>6</sup>

Many of the best-known solid electrolytes, such as garnet-structured Li<sub>7</sub>La<sub>3</sub>Zr<sub>2</sub>O<sub>12</sub> and sulfide Li<sub>10</sub>GeP<sub>2</sub>S<sub>12</sub> (LGPS), have crystal structures that minimize the activation energy for this ion hopping. These materials exhibit a relatively flat energy landscape, i.e., the energy variation between the starting and ending sites is small. In addition, the high Li concentration in these materials allows concerted migration of multiple Li ions to occur, which further lowers the energy barrier for diffusion.<sup>5</sup>

In this work, using *ab initio* molecular dynamics simulations and nuclear

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magnetic resonance spectroscopy, Hautier and co-workers found that  $\text{Li-Ti}_2(\text{PS}_4)_3$  (LTPS) exhibits a tracer diffusion coefficient significantly higher than current known superionic conductors, such as LGPS. In addition, impedance spectroscopy revealed LTPS has an ionic conductivity on the same order of magnitude as many superionic conductors. The high tracer diffusivity, pre-factor ( $D_0$ ), and conductivity make LTPS a notable standout among ion-conducting solid materials.

To understand the exceptionally fast ion diffusion in LTPS, Hautier and co-workers studied particular features of the structure. *Ab initio* molecular dynamics (AIMD) simulations, which observe real-time ion positions, revealed that Li ions do not sit on well-defined crystallographic sites in LTPS. Instead, Li appears to diffuse around the 3D interconnected Ti-P-S network, mainly sitting in large “pockets” of space in between crystallographic sites of ions. Local environment analysis of all available sites indicated that the crystallographic Li-ion sites are highly distorted and unfavorable for Li ion to occupy, compared with sites in typical lithium-containing sulfides.

Hautier and co-workers argue that this widespread distortion of the sites in the crystal structure of LTPS prohibits any

particular Li configuration from being favored—making a “frustrated” energy landscape. As a result of this smoothed energy landscape, the energy barriers for ion migration are lower for individual Li ion jumps. Further, Hautier and co-workers reason that the high pre-factor of LTPS is a result of a longer jump distance and a stabilized transition state, as the sites are entropically stabilized.

Although LTPS cannot be yet used as a solid electrolyte because of the presence of redox-active Ti, the work of Hautier and co-workers significantly advances the knowledge of fast ion diffusion in superionic conductors. Given the promise of the LTPS structure, new compounds can be designed by chemical substitution of Ti with non-redox active elements, such as Zr, as potential solid electrolytes for all-solid-state batteries.

Most significantly, Hautier and co-workers illustrate the importance and possibility of increasing the pre-factor to improve Li-ion conductivity. Recent studies suggest that decreasing the activation energy by increasing the anion lattice polarizability simultaneously decreases the pre-factor (known as the Meyer-Neldel rule),<sup>7</sup> leading to a limited gain in ionic conductivity.<sup>8</sup> Hautier and co-workers demonstrate a viable new di-

rection of increasing the pre-factor to achieve high diffusivity and high ion conductivity in solids, widening the opportunity for discovering new superionic conductors.

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