

Short communication

Bond valence analysis of structure–property relationships in solid electrolytes

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Abstract

Our augmented bond valence approach may be used to establish structure–property relationships in solid electrolytes, to identify the mobile species and to locate energetically favorable transport pathways for the mobile type of ions through the bond valence sum mismatch “landscape” created by the immobile substructure. Here ion transport pathways of crystalline and glassy Li⁺ ion conductors are analysed. Beyond the visualization of pathways the bond valence analysis also provides assessments of the relevant activation energies and thereby helps to clarify transport mechanisms and to identify promising novel ion conducting materials. The approach is particularly useful for the analysis of disordered systems such as ion conducting glasses, where particularly strong structure conductivity correlation has been identified.

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1. Introduction

Empirical relationships between the structure of an inorganic solid and its transport properties may help to rationalize the search for novel ion-conducting or mixed-conducting solids as well as the optimization of known structure types. Over the recent years, we have developed structure–conductivity relationships based on empirical relationships between bond length and bond valence (BV). Our augmented BV method systematically accounts for the bond softness [1,2], which greatly enhances its usefulness for identifying the mobile species in a structure and for locating energetically favorable transport pathways for this ion through the BV mismatch “landscape”. Beyond a visualization of pathways the BV analysis of crystal structures (or of local structure models from force–field simulations) also provides an assessment of the relevant activation energies [3–5]. Pathway models for crystalline and amorphous ion conductors with various mobile cations or anions can thus be analyzed to identify underlying general principles [6]. Local structure models for ion conducting glasses are accessible by reverse Monte Carlo (RMC) fitting. In this case, the BV analysis even permits to predict absolute conductivities from the relative volume of the

percolating BV pathways (i.e. regions with a sufficiently low BV mismatch) in the RMC model [7–9]. Here, we will discuss applications of the approach to systems that might be of interest as electrolytes or electrode materials in lithium batteries.

2. Theory

“Accessible” sites for mobile ions *A* in a local structure model are identified using empirical relationships between the bond length *R* and a so-called bond valence s_{A-X} :

$$s_{A-X} = \exp \left[\frac{(R_0 - R)}{b} \right] \quad (1)$$

as sites where the mismatch of the bond valence sum $V(A)$:

$$|\Delta V(A)| = \left| \sum_X s_{A-X} - V_{id}(A) \right| \quad (2)$$

over the s_{A-X} from all adjacent counterions *X* approaches the ideal valence $V_{id}(A)$ (i.e. its oxidation state). To enhance the chemical plausibility of the BV “energy landscapes”, $|\Delta V(A)|$ is complemented by minimum distance and soft coordination number constraints.

For calculations of ion transport paths, our softBV parameter set [1,2] bears a number of advantages over conventional BV

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parameters (c.f. [10] and references therein). The most prominent advantage is a systematic adjustment of the BV parameter b to the bond softness. This is essential in modeling the influence of the type (polarizability, etc.) of both the mobile species and its counterion on mobility. In contrast to conventional BV parameter sets softBV parameters moreover assume that not only the first coordination shell but all counterions up to a cut-off radius of 4–8 Å (depending of the sizes and softnesses of the ions) contribute to $V(A)$. Again this is indispensable for modeling transport paths as it avoids artifacts in the BV sum variation, when an ion moves across the border of its coordination shell.

BV models of transport pathways suppose that paths between accessible sites, along which $|\Delta V(A)|$ remains sufficiently low represent probable ion transport paths. Isosurfaces of fixed $|\Delta V(A)|$ for a certain ion type A thus may be approximately identified with regions that A can reach with a certain activation energy E_A . Regions of low BV mismatch that include both occupied and vacant sites enable local jumps of A , while a long-range transport requires pathways that extend through the whole structure. For crystalline phases this is equivalent to pathways that span the unit cell.

3. Results and discussion

3.1. Li_4GeS_4

Lithium transport pathways in the stoichiometric end member Li_4GeS_4 of the thio-LISICON family [11,12] have been calculated based on a structure redetermination by Murayama et al. [13]. Results are shown in Fig. 1. Even at low BV mismatch

thresholds, four Li(2) sites are connected with each other and with the Li(1) sites forming a complex network of sites in the b - c plane. Ion transport in solids requires a network containing both occupied and vacant sites for the mobile ions. As both Li(1) and Li(2) sites are nominally fully occupied, a low ionic conductivity along these pathways may occur only due to vacancies created by aliovalent impurities. At higher bond valence mismatch thresholds (c.f. the graph for $|\Delta V(\text{Li})|=0.09$ valence units (v.u.) in Fig. 1) an unoccupied local BV mismatch minimum (interstitial site) occurs in the center of the unit cell. As shown in the final graph of Fig. 1, a three-dimensional pathway exists at $|\Delta V(\text{Li})|=0.12$ v.u. that connects the Li(1)/Li(2) layers along the y -direction via the interstitial site forming a pathway suitable for DC conduction. However, the nearby local pathway region around Li(3) remains isolated from the infinite pathway even at rather high BV mismatch thresholds; Li^+ ions or vacancies on the Li(3) site will thus not contribute to the DC conductivity.

As the number of unoccupied sites within this pathway is rather low, it may be expected that stoichiometric Li_4GeS_4 exhibits only a low ionic conductivity. Since the PS_4 tetrahedra in Li_3PS_4 are arranged in a similar way as the GeS_4 tetrahedra (both compounds may be described as belonging to the γ - Li_3PO_4 structure type), while Li^+ sites and especially their occupancies differ, a disorder in the Li site distribution may be expected for the mixed crystals $\text{Li}_4\text{Ge}_{1-x}\text{P}_x\text{S}_4$. Therefore, these thio-LISICON phases will exhibit a significantly higher ionic conductivity along essentially the same transport pathways. (A more detailed analysis requires a local structure model of $\text{Li}_4\text{Ge}_{1-x}\text{P}_x\text{S}_4$.)

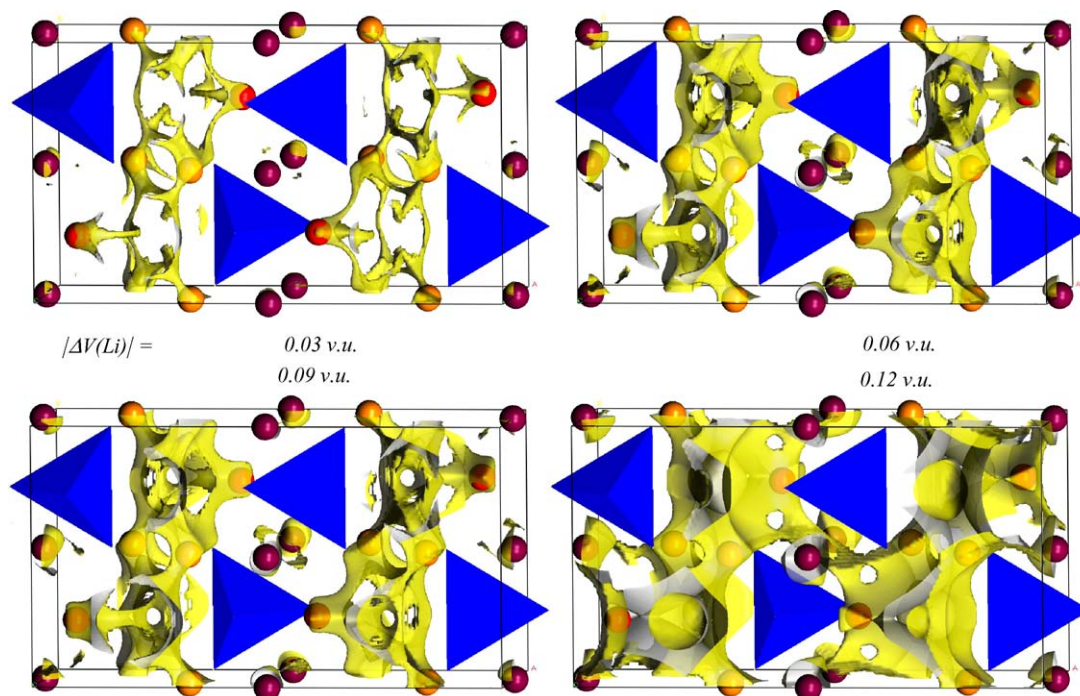


Fig. 1. Bond valence model of Li pathways in Li_4GeS_4 depicted as isosurfaces for different values of the Lithium BV mismatch $|\Delta V(\text{Li})|$ in the range 0.03–0.12 valence units. Li positions marked by spheres (Li(1): red, Li(2) orange, Li(3) dark red) (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of the article.).

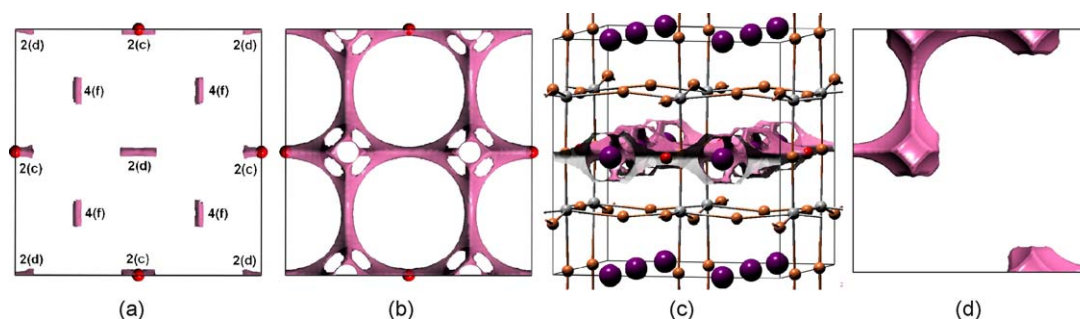


Fig. 2. $|\Delta V(\text{Li})|$ isosurfaces for different values of $|\Delta V(\text{Li})|$ values of (a) 0.1, (b and c) 0.3 and (d) 0.4 valence units, projected along the c -axis of the superstructure of $\text{La}_{0.62}\text{Li}_{0.16}\text{TiO}_3$ according to Yamada et al. [14]. Sites types for Li are identified in (a). (c) Location of the conduction plane in the structure. (d) Projection along c of a typical Li pathway based on a local structure model (with some of the La(2) sites occupied).

3.2. $\text{La}_{2/3-x}\text{Li}_{3x}\text{TiO}_3$

A recent neutron diffraction structure refinement for $\text{La}_{2/3-x}\text{Li}_{3x}\text{TiO}_3$ (LLT) with $3x \approx 0.16$ by Yashima et al. [14] provides a suitable starting point for modeling Li paths in LLT. A comparison of BV parameters of Li and La immediately shows that e.g. a Li on the La(1) site would have a valence of c.a. $2/3$ only. The extent of the BV mismatch in this case strongly favors the conclusion that Li prefers a different site than La. The superstructure proposed in [14] (nearly all La sites in one z -layer filled, while the next layer contains distinct La(2) and Li sites) makes it possible that both La and Li adopt a matching valence sum. Fig. 2 displays a BV model of the ion transport pathway. In Fig. 2(a–c) exclusion radii are applied to the (almost) fully occupied La(1) and Ti sites, but not to the La(2) atoms in the conduction plane with an occupancy of only ca. 0.3. According to the BV model LLT should (for $3x = 0.16$) exhibit a two-dimensional conduction involving jumps from the 2(c) equilibrium sites to a shallow local minimum at the 4(f) interstitial site and from there either to one of two deeper local minima 2(d) or to an additional 2(c) site. As each Li on a 2(c) site blocks two adjacent La(2) sites at a distance of 1.92 \AA , the 2(c) site cannot be fully occupied (which would correspond to $3x = 0.25$), as for $3x > 0.2$ not enough unblocked La(2) sites are left. This is no problem for $\text{La}_{0.62}\text{Li}_{0.16}\text{TiO}_3$, but it shows that this structure model cannot be the general solution for the whole range of x values in LLT. As long as 2(c) is the only equilibrium site for Li, mobile Li^+ can only hop to the few vacant Li^+ sites in $(V_{\text{Li}}2V_{\text{La}(2)})$ defect associates, so that there are not too many targets for $2(c) \rightarrow 2(c)$ hops. Thermal motion therefore leads to an additional occupancy of nominally vacant 2(d) and 4(f) sites in the same z plane, even if the energy of these sites is slightly raised, e.g. by their shorter distance to Ti.

While in the previous cases the structures were well-known, often a closer look at published crystal structures of solid electrolytes reveals that they are not sufficiently precise to serve as a basis of BV calculations. Therefore the first step of BV modeling is to check the plausibility of the crystal structure data and to search for a more plausible structure model (e.g. by optimizing the positions of light atoms in XRD structure determinations) so that the root mean squared average BV mismatch (the so-called “Global Instability Index”) is reduced to a plausible value. Details about the use of softBV parameters for GII-optimisations are given in [15]. A recent example in which

the crystal structure (including the space group) had to be revised before a meaningful pathway analysis could be performed is the garnet-related Li^+ conductor $\text{Li}_5\text{La}_3\text{M}_2\text{O}_{12}$ (M: Nb, Ta). Details about the optimized crystal structure and the pathway analysis have been published elsewhere [16]. Ion conductors with a significant disorder in the immobile substructure require a different approach. Here, local structure models are derived by combing crystallographic information with force–field simulations (see e.g. [17]).

3.3. Mixed conductors

In contrast to experimental measurements, BV modeling of ion transport in mixed conductors does not require special procedures, as electronic conduction processes will hardly affect the modeling for cation conductors (except for minute changes of cation–cation exclusion radii, when the oxidation state of the cations changes in the course of electronic transport processes). Models of the three-dimensional pathways in spinel-type LiMn_2O_4 and the zig-zag-shaped one-dimensional pathways in LiFePO_4 are given as examples in Fig. 3. The latter case may be of interest for a comparison with transport pathway studies from accurate determinations of anharmonic atomic displacement parameters, because the direction of the transport channels in LiFePO_4 does not coincide with the direction of the largest atomic displacement amplitude (which is determined by the shape of the local energy (or BV mismatch) landscape closer to the equilibrium site). The advantage of being able to model ionic conductivity even in predominantly electronic conductors also means that a compound that seems to be a fast ion conductor according to BV modeling still has to be tested for its electronic conductivity either experimentally or by computationally more demanding ab initio calculations. It may be also noted that effects of electronic processes are of greater relevance to anion conductors, for which fluctuations in cation valences translate into significant changes in the bond valence parameters.

3.4. Li conducting glasses

While ion transport processes in crystalline electrolytes may be traced back to a few fundamental mechanisms, a generally accepted transport model for fast ion conducting glasses is still lacking. This is largely due to the fact that the information from

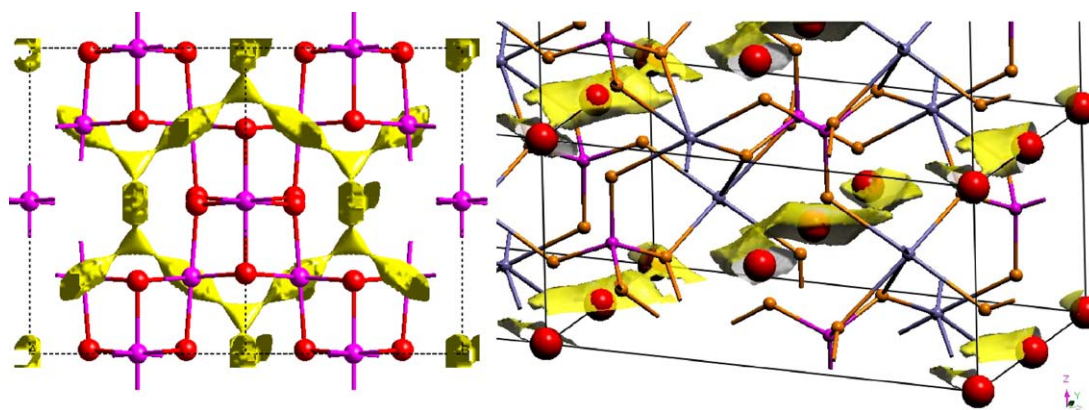


Fig. 3. BV model of Li pathways in spinel-type LiMn_2O_4 (left-hand side) and LiFePO_4 (right-hand side).

diffraction or spectroscopy data of amorphous systems is not sufficiently detailed to yield a unique structure model. The reverse Monte Carlo (RMC) technique at least permits to produce models that reproduce characteristic features of the structure and fully harmonize with all experimentally available information on the structure of the system (e.g. X-ray, neutron, EXAFS) [18]. Hence, RMC models may be used as a basis for the BV analysis of ion transport pathways. Fig. 4 shows ion transport pathways in the glass LiPO_3 as an example.

Due to the complexity of the pathways only a statistical analysis, e.g. based on percolation theory, can provide representative information on the characteristics of the ion transport in glasses. We found that the volume fraction of percolating ion conducting pathways determined from RMC structure models can be used to compare transport properties of different ion conducting glasses and permits the prediction of both activation energies and even

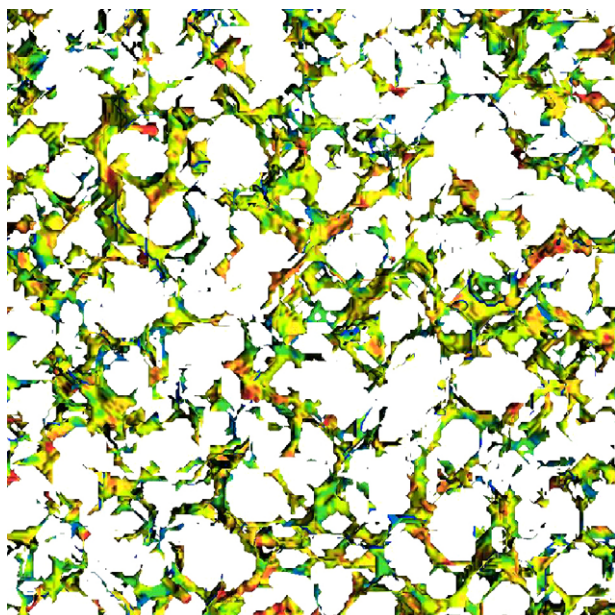


Fig. 4. BV model of Li^+ pathways in a RMC local structure model of the glass LiPO_3 . Rainbow colors indicate the coordination number of the Li in this pathway region (ranging from blue (CN < 4) to orange (CN > 6)) (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of the article.).

of absolute conductivities [7–9]. Due to the non-statistical distribution of the accessible volume (as well as of the mobile cations) a volume fraction of accessible regions of only a few percent is sufficient to ensure the existence of an infinite pathway.

The local dimensionality of the pathways is typically of the order of two (but varies systematically with dopant concentration or temperature) [10]. Thereby a rather low number of blocking ions can effectively reduce the conductivity, which proved to be a main factor causing the so-called mixed alkali effect [8,9]. The comparison of the number of mobile ions to the number of suitable sites (with a sufficiently small matching BV difference, a matching coordination number and a sufficient distance from the nearest site) shows that different glasses exhibit different ion transport mechanisms: in oxide glasses the number of suitable sites for the larger alkali ions hardly exceeds the number of ions so that the ionic motion becomes more vacancy-like, while e.g. in halide doped Li^+ and Ag^+ there is a sufficient number of unoccupied suitable sites.

Recently, we have started to combine RMC and MD simulations and analyzing MD trajectories based on RMC configurations. This yields a quantification of the dependence of pathway characteristics on time and temperature. The approach thus helps to clarify transport mechanisms and to identify promising novel ion conducting materials [3,8].

4. Concluding remarks

The bond valence analysis is a simple yet useful tool for the identification of ion transport pathways in both crystalline and amorphous ion conductors. Thereby BV calculations can help to understand the structural prerequisites for materials with a high ionic conductivity and provide guidelines in the search for promising novel classes of solid electrolytes or of mixed conducting electrode materials.

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