

Sodium-Ion Technology

On the Way to New Possible Na-Ion Conductors: The Voronoi-Dirichlet Approach, Data Mining and Symmetry Considerations in Ternary Na Oxides

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Abstract: With the constant growth of the lithium battery market and the introduction of electric vehicles and stationary energy storage solutions, the low abundance and high price of lithium will greatly impact its availability in the future. Thus, a diversification of electrochemical energy storage technologies based on other source materials is of great relevance. Sodium is energetically similar to lithium but cheaper and more abundant, which results in some already established stationary concepts, such as Na-S and ZEBRA cells. The most significant bottleneck for these technologies is to find effective solid ionic conductors. Thus, the goal of this work is to identify new ionic conductors for Na ions in ternary Na oxides. For this purpose, the Voronoi-Dirichlet approach has been applied to the Inorganic Crystal Structure

Database and some new procedures are introduced to the algorithm implemented in the programme package ToposPro. The main new features are the use of data mined values, which are then used for the evaluation of void spaces, and a new method of channel size calculation. 52 compounds have been identified to be high-potential candidates for solid ionic conductors. The results were analysed from a crystallographic point of view in combination with phenomenological requirements for ionic conductors and intercalation hosts. Of the most promising candidates, previously reported compounds have also been successfully identified by using the employed algorithm, which shows the reliability of the method.

Introduction

With the beginning of the 21st century, our lives have become more and more electrified. Mobile phones and cars are mobile electronics that have been rendered possible only by the use of electrochemical energy storage devices due to their high energy densities and technological maturity. Battery and accumulator research and technology are ever-increasing fields that span from basic scientific questions of chemistry and physics to a broad range of applications and engineering. Fossil fuel sources are limited and research is focussed on natural regen-

erating resources that need stationary energy storage to compensate for the capriciousness of, for example, wind and sun.^[1]

The biggest up-to-date player in mobile electrochemical energy storage is the lithium-ion battery. Lithium has, apart from hydrogen, the highest gravimetric energy density, which is one of the most important factors for mobile applications. For stationary batteries, however, the price per stored amount of energy is the most determining factor. In this regard, sodium is more favourable than lithium due to its higher abundance. Moreover, sodium seems advantageous as far as safety issues are concerned.

For this reason, today's high-temperature sodium-based batteries, especially sodium-sulfur and sodium-nickel-chloride (ZEBRA or Zeolite Battery Research Africa) cells, are the most important stationary accumulators.^[2] Both chemistries incorporate two liquid active masses in their respective electrode compartments, connected by a solid electrolyte of high ionic conductivity called a super-ionic conductor. The solid electrolyte is usually made of Na β'' -alumina and acts as a physical and electronic barrier between the two electrodes.^[3]

A promising approach is to adapt and transfer the existing low-temperature lithium technologies to sodium-based cells and to optimise them for lower temperatures. One of the major challenges is to adapt the ionic conductor to these new conditions. Because ionic conductivity strongly decreases with decreasing temperature, the thickness of the solid electrolyte

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Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/chem.201501975>.

should be reduced. This adjustment, however, results in a strong deterioration of the mechanical properties of the commercially available high-temperature solid electrolytes. Therefore, more easily depositable electrolytes and new materials for the intercalation of sodium ions have to be identified. In this search, the role of theoretical tools with high predictability is increasing.

Crystallography is a powerful tool not only for the description but also the prediction of crystalline matter. Intercalation as a topochemical reaction—the host structure stays more or less unchanged during insertion and removal of the intercalated species—can be easily described as the addition of an ion on a crystallographically empty or partially occupied site. For the whole crystal to accommodate a maximum number of ions, diffusion between these sites needs to be possible. In this way, crystalline solid ionic conductors can be described similarly to intercalation hosts. Generally speaking, if a crystal structure has interconnected voids that can host an ionic to-be-conducted species, it should be able to act as a conductor as well. This idea is the basis of the application of the Voronoi–Dirichlet approach to describe and find new solid electrolytes,^[4] it has already been successfully applied for Li-ion conductors.^[5] Based solely on geometry, it offers a very fast algorithm and allows the analysis of thousands of compounds within an hour.

There are, of course, other well-established approaches, such as the bond valence methodology (BVM), which correlates bond lengths with their strength to identify voids to host ions and can be equally applied to large databases.^[6] BVM enables the calculation of force fields and even allows calculation of practically important parameters, for example, activation energies.^[7] It becomes an especially powerful tool for understanding the behaviour of single compounds in depth.^[8] However, an automated calculation of one structure will take a couple of minutes and can give very similar results to Voronoi–Dirichlet partitioning. Hirshfeld and procrystal analysis of crystal structures can be another valuable tool to identify void systems in crystal structures in a mixed energetic and geometric way. Again, an analysis of one structure can be performed in a matter of minutes.^[9] All of these methods originate from structure verification and topology identification.

This report will cover the Voronoi–Dirichlet methodology for Na⁺-ion conductors restricted to ternary sodium oxides. A new method for channel radius determination is presented and the whole methodology is now based on newly determined, data mined structure parameters. A crystallographic systematisation and evaluation is presented subsequently.

General Principles

The Voronoi–Dirichlet approach describes a method of partitioning space. A Voronoi–Dirichlet polyhedron (VDP) around a given point i in an assembly of N points ($i, j \in N; i \neq j$) is generated by constructing planes perpendicular and midway to all inter-centre line segments ij ; the smallest polyhedron is the VDP of the point i . Each additional point that lies inside this construct is closer to point i than to any other point j . This method can also be applied to atomic structures by inter-

changing each point with an atom or ion (for the sake of readability, the terms atom and ion will be subsumed to a generic atom). The Voronoi–Dirichlet polyhedron of an atom in a structure is characterised by its vertices, edges, faces and volume.^[10] The volume can be used to describe the size of this atom in the crystal structure, a measure for its atomic radius. The size of a face of a VDP is proportional to the strength of the chemical bonding to a neighbouring atom. The closer a neighbour, the larger a face and the higher the attractive force between the central atom and its neighbour and thus, the stronger the bond. By finding the atoms that share the largest faces of a VDP, the nearest neighbours are identified. According to Ref. [10], the face sizes can also be described by solid angles Ω .¹ The vertices of a VDP describe possible voids in the structure because they are farthest away from all surrounding atoms. Each vertex is connected to neighbouring vertices through VDP edges. These edges are, just like vertices, the farthest away from their (usually) three constructing atoms. They can thus be regarded as channels between these voids (see Figure 1).

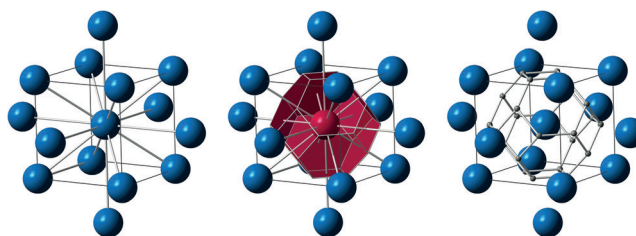


Figure 1. Graphical representation of the Voronoi–Dirichlet method. Left: The Γ partial structure of AgI (i.e., a bcc arrangement) is depicted. Middle: The Voronoi–Dirichlet polyhedron around the central atom (red). The vertices represent structure-immanent voids, the edges indicate connecting channels. Right: The ionic conduction channel system for the Ag⁺ ions is shown.

By constructing secondary VDP around the vertices of the primary VDP, the space that is assigned to this void can be determined and thus, atoms can be identified that could theoretically occupy this space. If neighbouring voids can host the same atom, there will be a VDP edge connecting them. By analysing the space between the constituting atoms, the edge can be evaluated as a potential diffusion path between these two voids.

The programme ToposPro, a multifunctional tool for crystallographic analysis, allows to identify new potential ionic conductors by application of the Voronoi–Dirichlet method.^[11] It introduces a set of geometric parameters for the numerical evaluation of VDP volumes, faces, edges and vertices. For the analysis of ionic conductivity, the most important values are then r_{SD} , G_3 and r_{Chan} .^[4,5] r_{SD} is the radius of a spherical domain (SD) that has the same volume as the considered VDP, which is a measure of the atomic size in the structure. G_3 is the second

¹ Each vertex of a VDP face is projected on a unit sphere around the central atom to give a segment of the sphere. Its percentage (projected face surface area to unit sphere area) is the solid angle.

moment of inertia of the VDP, which is a measure for the sphericity of the VDP; the smaller this value, the more spherical the VDP.^[10] r_{Chan} is the channel radius and describes the channel size between two voids. An algorithm was introduced in the new version of ToposPro: The radius of a circle passing through the three channel-constituting atoms is taken as a more sensible assumption to determine this value.^[11]

The most important factor for both voids and channels is their significance, which is connected to two conditions:^[4]

- 1) Determination: Both voids and channels need to be determined only by anions, that is, oxygen in the case of ternary oxides. If one of the constituting atoms is a cation, Coulomb repulsion will give an energy barrier too large for another cation to enter this site or channel.
- 2) Comparison: The geometrical data of the voids and channels is compared to a set of expected values. That is, r_{SD} and G_3 need to be at least as large as/smaller than the data mined values for Na in the O environment. For the channel radius, the data mined average Na–O distance is considered.

Only if both conditions are fulfilled is the determined void-channel system consistent with the VDP approach.^[5] For more information on the technical details, see the Supporting Information.

All the important steps for this methodology, including future testing of the newly identified materials, are summarised in Figure 2.

Results

Data mining

As a basis for this work, the Inorganic Crystal Structure Database (ICSD; release 2014/1) with 170 387 compounds was used.^[12] The most important values for this work (r_{SD} , G_3 and r_{Chan}) relate to sodium with oxygen nearest neighbours because Na^+ as a cation moves through a channel composed of O^{2-} anions for the compounds in question. Accordingly, 9797 compounds comprised of at least Na and O were extracted from the ICSD. After a thorough revision procedure (e.g., removal of duplicates and entries with inconsistent chemical formulae), which is described in the Supporting Information, several thousand items were rejected to give a set of 4758 entries.

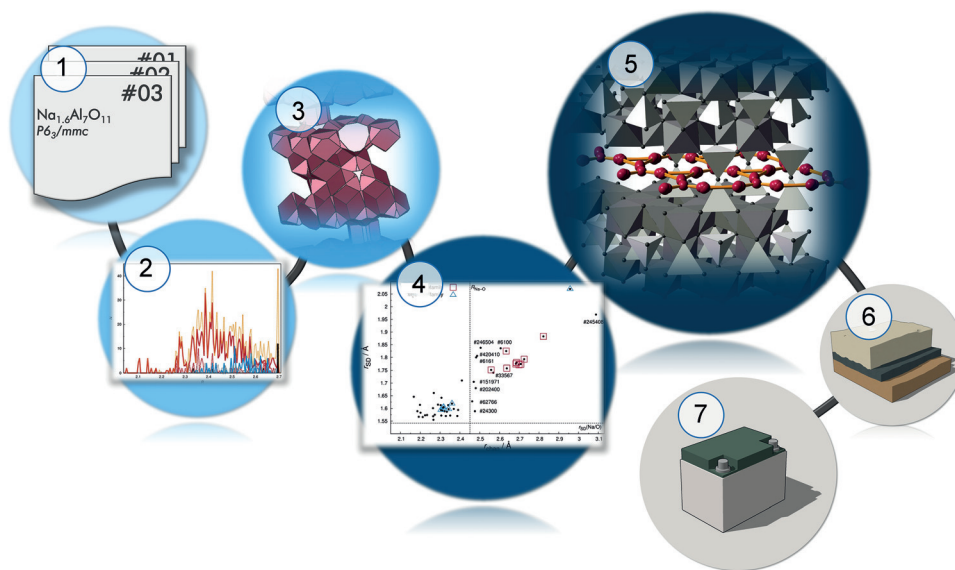


Figure 2. Graphical summary of all necessary steps for the Voronoi–Dirichlet approach: Use of a database (1) for data mining (2). The Voronoi–Dirichlet partitioning (3) is then applied and the data mined values (4) are used to determine potential Na-ion conductors/intercalation hosts (5). Experimental work (6) should then follow to see if the material qualifies for electrochemical storage technology (7).

It was found that sodium offers a large variety of coordination numbers with oxygen, which is considered beneficial for ionic conduction because coordination number changes can occur during ion migration. For the data mining, however, this is disadvantageous because different coordination numbers show different average sodium–oxygen distances ($R_{\text{Na-O}}$). A mean value is chemically not correct, albeit necessary to determine the significance of the channels. Therefore, the arithmetic average value of all sodium–oxygen distances in all sodium-containing oxides was calculated. An average distance of $\bar{R}_{\text{Na-O}} = (2.45 \pm 0.13) \text{ \AA}$ was determined. Technical details are summarised in the Supporting Information.

Another important value is the smallest solid angle Ω_{min} , which can still be taken as indicative of an attractive interatomic interaction or a strong bond.² From an analysis of all contacts between Na and any other element that is not oxygen in the revised database, a clear boundary is found at $\Omega_{\text{min}} = 1.5\%$, which separates strong contacts from weak contacts. This value is comparable with the one presented in Ref. [10].

On determining r_{SD} , three compounds were identified that had very high values because of large intrastructural cavities that hosted Na^+ ions. They were omitted during the data mining process because these ions show a very different chemical surrounding compared with most other sodium ions. The arithmetic mean value of r_{SD} was calculated for all remaining compounds: $\bar{r}_{\text{SD}}(\text{Na/O}) = (1.54 \pm 0.09) \text{ \AA}$. The second

² In this context, a strong interaction means intramolecular bonds, that is, metallic, ionic or covalent bonds. VDP cannot be used to discriminate between these bonding types. Weak interactions, in this context, refer to all intermolecular bonds, such as Van der Waals and hydrogen bonds.

moment of inertia amounts to $\bar{G}_3(\text{Na/O}) = (82.8 \pm 2.5) \times 10^{-3}$. These new values are in very good agreement with Ref. [10].

Voronoi–Dirichlet partitioning

The above-mentioned revised database was consequently used. Additionally, from these 4758 items, 1232 that contained either Li or H (and deuterium) were neglected because these compounds would tend to show Li^+ or H^+ conductivity due to their chemical similarity to Na and smaller ionic radii. Eventually, of the remaining 3526 entries, all 565 ternary sodium oxides, that is, $\text{Na}_x\text{M}_y\text{O}_z$ with M other than Li, H and D, were extracted.

After the construction of VDPs to create a system of all possible voids and channels, their significance was checked. The first step was to screen all the void environments for cationic constituting partners with solid angles higher than Ω_{min} to remove these. These cations would be strongly bonded to Na in the void position and, thus, the void cannot be a Na-ion host due to Coulomb repulsion. Furthermore, if there are only O environments for voids, all channel-constituting atoms will be O as well. 266 out of 565 compounds without any remaining physically meaningful voids were deleted.

Subsequently, all r_{SD} values for all voids in all compounds were checked against the data mined value. If the voids have larger r_{SD} values, they are considered to be possible Na^+ hosts. Compounds exhibiting only smaller voids were deleted because they are presumed to show no ionic transport. A similar procedure was performed for the G_3 values. Eventually, a further 119 items were deleted.

The channel radius is the bottleneck for ionic migration. If it is larger than the average Na–O distance ($\bar{R}_{\text{Na-O}}$), the channels are considered as potential conduction paths. A tolerance factor of 15% was added to allow for some general structural elasticity and to consider that some channels impenetrable at room temperature may open for ionic migration at slightly elevated temperatures.^[4] With this tolerance factor, a reference of $\bar{R}_{\text{Na-O,ref.}} = 0.85 \times 2.45 \text{ \AA} = 2.083 \text{ \AA}$ was calculated and channels smaller than this reference were deleted. Remaining isolated voids, that is, voids not connected to others and voids connected to only an adjacent one were also deleted. If this resulted in removing all voids, such compounds were deleted as well. After this final step, the database still held 131 entries.

Taxonomy

Each remaining candidate was analysed separately after the dimensionality of its void/channel network was determined by using ToposPro. Finally, the resulting compounds were classified as having 0D (77 entries), 1D (25 entries), 2D (22 entries) and 3D channel systems (5 entries). There were two crystal structures that showed promising results, however, the Na atoms in the channels were partially substituted by other elements. These compounds were neglected because the substituted atoms could close the channel and hinder diffusion. An example of this mechanism is the system LiNiO_2 , characterised by NiO_2 layers between which Li can be intercalated. However,

Ni can enter the gaps as well, which closes the space between the slabs.^[13,14]

A graphical representation of the results is shown in Figure 3. For systematisation purposes, the newly identified Na^+ electrolytes/intercalation hosts, including the 0D systems, that is, those without percolating channels, were categorised with respect to their crystal system. The periodic table in Figure 6 indicates which elements have been found in which conduction system.

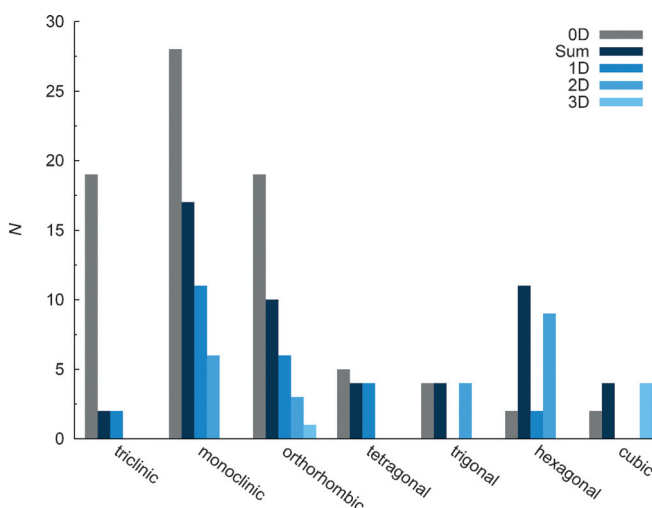


Figure 3. A number of compounds with 0D, 1D, 2D and 3D systems of channels, and the sum of the latter three, categorised according to their crystal system.

A graphical analysis of the r_{SD} and r_{chan} values is provided in Figure 4, which shows 52 high-potential candidates for solid ionic conductors. Based on the assumptions made in Ref. [4], all compounds beneath $0.9 \cdot \bar{R}_{\text{Na-O}}$ are most probably only ion-

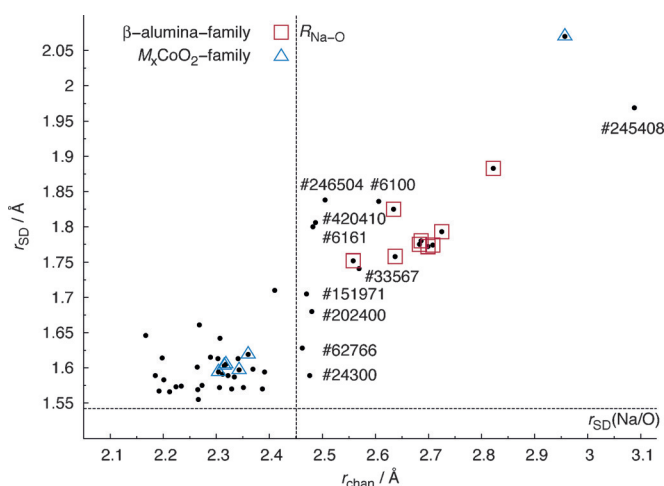


Figure 4. Graphical summary of all 52 newly identified compounds in relation to their r_{SD} and r_{chan} values. Larger voids indicate larger channels connecting them. The two most prominent families and the thresholds of $\bar{R}_{\text{Na-O}}$ and $\bar{r}_{\text{SD}}(\text{Na/O})$ are marked. The ICSD numbers are referenced for compounds with the largest voids and channels apart from the β -aluminas.

conducting at higher temperatures, those between 0.9 and $1 \cdot \bar{R}_{\text{Na-O}}$ may conduct at moderate temperatures, whereas those higher than $\bar{R}_{\text{Na-O}}$ should give promising conductivities even at room temperature.

Discussion

Sodium–alumina compounds constitute the best Na-ion conductors of today and are widely used in liquid sodium-anode batteries. On the one hand, the fact that the method of Voronoi–Dirichlet partitioning identifies these sodium–alumina compounds from 3526 compounds taken from the ICSD is very promising, and this family of compounds shows the largest voids and connecting channels. On the other hand, because this material has already been successfully identified as a super-ionic conductor in the past, its crystal structure has been intensively investigated. This is an inherent difficulty in finding new possible functional materials within a crystallographic database; materials with functions that have been discovered in different ways will show up frequently if crystal structure analyses were commonly carried out. Many others with interesting structures or modifications may never have been of interest and thus their crystallographic structures have never been determined. In this way, data mining can be a self-fulfilling prophecy. Generally speaking, the larger and more general a database, the better it is for the data mining approach.

The Voronoi–Dirichlet method is only applicable for interstitial and vacancy mechanisms that do not alter the structure during ionic jumps. Furthermore, a crystal structure that has atomic coordinates of each constituent is needed. In theory, amorphous materials and compounds that contain grain boundaries could be analysed as well, but they do not have structures that are as easily describable as crystalline solids.

Symmetry

To systematise the identified materials and provide some parameters for the assessment and ranking of new ionic conductors and intercalation hosts, symmetry considerations are presented below.

More than 63% of the identified compounds exhibit neither a triclinic nor a monoclinic crystal system (see Figure 3). These compounds seem to favour closed loops, that is, they show trapped ions, and fewer infinite³ channels in the structure. Al-

though the overall number of candidates is comparably small for a sound statistical evaluation, compounds with 1D channel networks are mainly found in orthorhombic and tetragonal systems. Hexagonal and trigonal systems are prominent for compounds with 2D channel networks. Quite often, these compounds are characterised by a packing of equivalent slabs between which the potentially mobile cations are inserted. The most prominent compound that shows this feature is graphite, which is an excellent intercalation host for all kinds of ions, including Na^+ .^[15] Compounds with 3D conduction networks ideally need a crystal system that features symmetric and metric equality in all three directions in space. 80% of the compounds identified as having a 3D conduction network are characterised by a cubic system.

Similarly to the discussion of physical properties according to Neumann's principle and to reduce complexity, we focus on the 32 crystallographic point groups for discussing symmetry relations. For this purpose, Figure 5 summarises all group–subgroup relations important for this study. The 2D conducting compounds in particular show a clear relationship to the high-

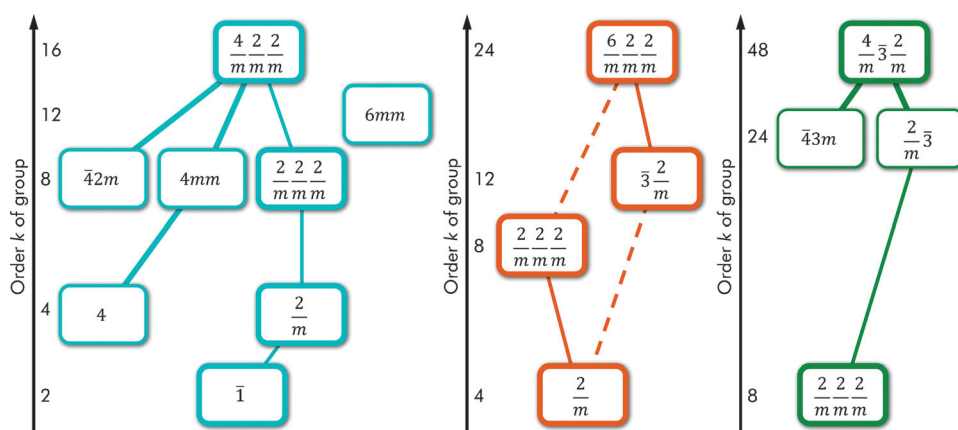


Figure 5. Group/subgroup relations for the high potential compounds with 1D (blue, left), 2D (orange, middle) and 3D (green, right) channel systems.^[20] Full Hermann–Mauguin symbols are used. The highest symmetrical group in its respective crystal system is framed by thick lines. Point groups that belong to one crystal system are connected to each other by thick lines. Full lines indicate normal and dashed lines conjugated subgroups. 1D systems show a relation to $\frac{4}{m} \frac{2}{m} \frac{2}{m}$ as their highest supergroup, 2D to $\frac{6}{m} \frac{2}{m} \frac{2}{m}$ and 3D to $\frac{4}{m} \frac{3}{m} \frac{2}{m}$.

est symmetry hexagonal group $\frac{6}{m} \frac{2}{m} \frac{2}{m}$. Those examples that do not adopt the hexagonal holoedry have a direct subgroup relation that is either normal in the case of $\frac{3}{m} \frac{2}{m}$ or of conjugated character in the cases of $\frac{2}{m}$ and $\frac{2}{m} \frac{2}{m} \frac{2}{m}$, which share a normal subgroup relation themselves. The basic principle is the hexagonal symmetry and its stacking of symmetrically equivalent slabs along the [001] direction. Similarly, in 3D channel network compounds the basic principle is equality in all directions, which holds for all cubic point groups. The point group $\frac{2}{m} \frac{2}{m} \frac{2}{m}$, which is also observed in our study for a 3D channel network compound, shows lower symmetry but is related to the cubic point groups by a normal subgroup/supergroup relation to $\frac{2}{m} \frac{3}{m}$.

A cubic material showing ionic conduction will be a 3D conduction compound because of its sets of symmetrically equivalent, non-coplanar symmetry directions. The relationship between the point groups found for 1D channel systems is not

³ In this context, infinite describes channels that travel through the whole crystal structure; circles are excluded from this. Thus, a percolation is achieved.

as clear as for the 2D and 3D conduction channel compounds. The point groups are more spread showing as the highest-order point group $\frac{4}{m} \frac{2}{m} \frac{2}{m}$.

In accordance with Neumann's principle, the dimensionality of the void network, that is, the ionic conductivity, is included in the point-group symmetry of the host crystal structure. For 1D channel system compounds with a tetragonal crystal system, the conduction channel is parallel to the principal symmetry direction [001]. Even though there is no direct relationship between the hexagonal point group $6mm$, which is exhibited by two compounds, their conduction channel is also parallel to the principal symmetry direction [001]. For all other hexagonal compounds, a 2D conduction channel network normal to the principal symmetry direction is observed; the channels are parallel to the second symmetry direction. Generally speaking, the conduction channel seems to be situated along the principal symmetry direction or normal to it.

In references [13,16], the authors explain that close-packed O structures are the most fitting ionic conductors/intercalation hosts because they exhibit connected tetrahedral and octahedral interstitial sites that are large enough for guest metal ion insertion. This theory is similar to the one used in the approach explained in this article. Here, a more general void that can be of random shape is assumed. The more ideal a close-packed oxygen sub-lattice, the higher the possibly achievable symmetry. Furthermore, the more symmetrical the surrounding of a void, the more equal the channels that connect these voids. By adding highly symmetric voids and their surrounding to a virtual crystal structure, either a highly symmetric crystal structure or a structure with lower point group symmetry but high local symmetry environments of interconnected voids is obtained. Thus, more important than general symmetry is the local symmetry of the void site which can be independent of the whole structure. SiO_4 tetrahedra, for example, can also be present in point groups with lower symmetry than 23 and even in amorphous compounds.

Symmetry can, to a certain extent, be taken as a measure to evaluate the energetic landscape of a given atomic arrangement. The higher the point group symmetry, the more symmetrically and, therefore, energetically equivalent sites can be generated. If there are many sites of the same (low) energy connected to each other, ionic conduction is ameliorated. Thus, high point group symmetry structures should show better conductivity than lower symmetry derivatives. However, if the chemical environment of different voids is symmetrically similar and the rest of the structure is not, the energy of these atomic positions can be equal as well. Sites of equivalent local symmetry are achieved in high-symmetry crystal structures (which leads to 2D and 3D conducting compounds) but also in lower-symmetry structures if the chemical environment allows for such sites. This, however, may lead to 1D or even 0D channel systems in which these sites are not well connected to each other (low symmetry enforces no isotropy).

ToposPro has broad applicability, particularly for topologies and interatomic relations. It is ideally suited to analysing the local atomic environment of atoms on specific Wyckoff sites. The Voronoi–Dirichlet method has the disadvantage that com-

plex polyhedra can be constructed that create void clusters. Until now, a reliable merging algorithm has not been implemented and the (manual) analysis of multi-site voids is not feasible for a high-throughput methodology. However, this is a work in progress and will be published elsewhere.

Elements

All elements M observed in $\text{Na}_x\text{M}_y\text{O}_z$ compounds with 1D, 2D, 3D and 0D channel systems have been summarised in Figure 6. The most frequently observed elements for potential Na-ion conductors are aluminium (7 compounds), titanium (5),

H																	He
Li	Be											B ⁻⁵	C ⁻¹	N ⁻¹	O	F	Ne
Na	Mg											Al ⁶	Si ⁻⁸	P ⁻⁵	S ⁻¹	Cl ⁻¹	Ar
K	Ca	Sc	Ti ²	V ⁻³	Cr ⁻²	Mn ⁻²	Fe ⁻³	Co ²	Ni	Cu ⁻¹	Zn	Ga	Ge ⁰	As ⁻¹	Se ⁻¹	Br	Kr
Rb	Sr	Y	Zr ⁻¹	Nb ⁻¹	Mo ⁰	Tc	Ru ¹	Rh	Pd	Ag	Cd	In ⁻¹	Sn	Sb ³	Te ¹	I	Xe
Cs	Ba		Hf	Ta	W ⁻⁶	Re ¹	Os ¹	Ir	Pt ¹	Au	Hg	Tl ⁻²	Pb ⁰	Bi ¹	Po	At	Rn
Fr	Ra		Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg							
			La	Ce ⁻¹	Pr ²	Nd	Pm	Sm	Eu	Gd	Tb ²	Dy	Ho	Er ⁻¹	Tm	Yb	Lu
			Ac	Th	Pa	U ⁻¹	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

Figure 6. Periodic table with the elements M in $\text{Na}_x\text{M}_y\text{O}_z$ that give only 0D (red), mainly 0D (yellow), mainly non-0D (blue) or only non-0D (green) compounds. The given superindices indicate the sum of identified compounds for 0D (negative) and non-0D (positive).

cobalt (4) and niobium, ruthenium and antimony (3 each). From the VDP methodology, it is suggested that transition metals and, in general, elements of high valence in combination with oxygen are of high relevance. Of course, aluminium forms a large variety of compounds, many of which have already been investigated thoroughly, for example, the β - and β'' -alumina Na-ion conductors.

Silicon (8 compounds), phosphorus (6) and boron (5) in particular show 0D channel networks in ternary compounds. Their bonds with oxygen are usually of a covalent nature. These partners can build up infinite networks by corner-sharing (B, Si, P)O₄ tetrahedra to create intertwined chains. In these frameworks, large holes in which other atoms or ions are inserted can be present. These cavities are not connected to each other because the connecting voids are too small. If the chains are substituted by transition metals, the void volumes can increase, which creates infinite and thus percolating paths in the structure. Particularly for Li-ion conductors, this has already been proposed, for example, in Ref. [17].

Evaluation of ionic conductors/intercalation hosts

The necessary traits for good intercalation materials are given in Ref. [13]. They can be used to determine whether the identified compounds are eligible either as intercalation hosts or ionic conductors. The following requirements apply for both types of materials: 1) the materials should allow for the (rever-

sible) insertion/removal of ions without structural changes; 2) the insertion/removal process should be fast; 3) the materials should be stable during the different processes; 4) the materials should be low cost; and 5) the materials should be environmentally benign. For intercalation hosts there are three further necessities: I) there needs to be a suitable redox system; II) the insertion/removal reaction should either have a high or low free energy, which translates into a high (positive electrode) or low (negative electrode) redox potential; III) the material should have a good electronic mobility to conduct electrons to or from the redox system. For solid electrolytes, these conditions are mostly inversed: i) there is no need for reducible/oxidisable ions in the structure; ii) the insertion/removal process should not change the free energy of the material; iii) the material should be an electronic insulator to avoid the direct transport of electrons between the electrodes. Unfortunately, most of these features cannot be extracted from the ICSD. In fact, only I) and i) can be analysed by using the database, most of the other parameters can only be determined experimentally. If *M* offers a variety of oxidation states (see Ref. [18]) and can thus be reduced or oxidised, this is emphasised by the parameter *MV* given in Table 1 and the tables in the Supporting Information.

Table 1. The as-identified most promising candidates for solid electrolytes and intercalation compounds for candidates with non-0D channel systems. Listed are the respective chemical formulae, the space group, the dimension of the channel network, the crystallographic direction of the network and the multivalency of *M* (*MV*; multivalent = *y*), along with a relevant reference, if found, to the electrochemistry.

Formula	Space group	Dimension	Direction	ICSD#	<i>MV</i>	Ref.
Na _{1.29} SbO ₃	<i>Im</i> $\bar{3}$	3D	<111>	6100	<i>y</i>	
Na ₂ PrO ₃	<i>C2/c</i>	1D	[001]	154706	<i>y</i>	
Na _{1.68} Al ₁₁ O ₁₇	<i>R</i> $\bar{3}m$	2D	(001)	201178	<i>n</i>	[21]
Na ₂ MoO ₄	<i>Fddd</i>	3D	<100>	151971	<i>y</i>	[22]
Na _{0.384} CoO ₂	<i>P6₃/mmc</i>	2D	(001)	155510	<i>y</i>	[23]
NaNb ₃ O ₈	<i>Pmnm</i>	1D	[001]	202400	<i>y</i>	

From the viewpoint of the Voronoi–Dirichlet method, the most promising results should be obtained from compounds with high r_{SD} and r_{Chan} values and a high coincidence of identified voids and structure-immanent Na-sites. Furthermore, a good solid ionic conductor has a large amount of available sites of similar energy that are not fully occupied.^[19] These energies cannot be calculated by using the Voronoi–Dirichlet partitioning. Each site is, however, described by its Wyckoff-symbol, which carries information about symmetry and multiplicity, that is, the number of symmetrically equivalent positions in the structure that are also energetically equivalent. For structures with fully occupied sites, conduction is only possible by energetically unfavourable coordinative movements. To create a good conduction path, low occupancies are beneficial because these paths can more easily be entered by the migrating ions. To maximise the amount of conduction ions, crystal structures with high multiplicities and low occupancies of these conduction ions should be considered.

For intercalation hosts the idea remains the same. As intercalation will fill up all voids in the end, the sites do not necessarily need to be partially occupied but high multiplicities will allow high intercalation levels if all of the Na ions in the structure are mobile. Ions located on the same Wyckoff site will have the same energy, which translates to a steady slope in electrochemical potential. Na ions not taking part in the intercalation process will lower the capacity. The *M* element needs to be multivalent.

The most promising identified Na_{*x*}M_{*y*}O_{*z*} compounds are summarised in Table 1. The complete list is found in the Supporting Information.

The best-known ionic conductor for sodium ions is β'' -alumina, the trigonal variant of the hexagonal β -alumina. Both compounds were successfully identified by using the Voronoi–Dirichlet method. The hexagonal variant shows slightly larger void sizes (1.3%) and channel radii (3.8%), which leads to an assumed superior theoretical conductivity. The trigonal variant, however, exhibits better conductivities. This can be explained as follows: In the hexagonal β -alumina, Na occupies very high symmetric sites with low multiplicities (two times two in the case of ICSD reference code # 66561). In the trigonal β'' -alumina however, only one site is occupied that has a very high multiplicity of 18 (see ICSD reference code # 74473) within a similar unit cell volume. It shows more sites with a comparable and low occupancy and should, therefore, perform better than β -alumina.

Some of the compounds identified by using the Voronoi–Dirichlet method have already been researched and reported, most prominently the aforementioned β - and β'' -aluminas, the Na_{*x*}CoO₂ family, which has already seen use in lithium-ion batteries, and the various sodium titanias. A more detailed view of the results is given in the Supporting Information, which includes a list of data for the 52 most promising materials in a spreadsheet format. The structures of some compounds have not been determined at room temperature, but they cannot yet be discarded by using ToposPro. Until now, the identified antimonates and vanadates in particular have not been mentioned in Na-oriented literature, although the latter is already known for its Li-ion intercalation, which points to possible Na-intercalation and could thus be interesting for further research. The aluminas and cobaltates show the best results of all the compounds and should be studied, if they had not already been.

Conclusion

The Voronoi–Dirichlet method was used to find new potential Na-ion conductors and/or intercalation hosts on the basis of possibly free volumes in known crystal structures. 52 ternary Na_{*x*}M_{*y*}O_{*z*} candidates were extracted from the ICSD database. Some known solid electrolytes can be found among these structures, which have already been reported in literature in the context of Na⁺ conductivity. This is a clear indication that the general idea of the method allows for the identification of actual conductors and intercalation materials. Apart from possible structure-immanent voids and connecting channels,

a number of other parameters should be taken into account to evaluate the results of the method. Occupancies and multiplicities of Na ions in the structure can be used to further analyse each compound. Some symmetrical principles could be identified: 1D-conduction materials are most prominent in materials with a preferential axis, as found in the tetragonal crystal class. 2D compounds are found in hexagonal and rhombohedral crystals, and 3D conduction compounds can be identified with cubic structures in which all three main directions are equal. The most promising compounds determined by this method are the known β -aluminas and cobaltates, as well as the newly suggested antimonates and titanates.

The next important step for this algorithm is the implementation of merging of void clusters to make better predictions for less-symmetric compounds. This also allows for a broader applicability for more complex systems and a more in-depth analysis of the local structure of a void, that is, its atomic environment. This is the most important factor for ionic conduction because it generates the right surrounding for possible jumps from and into this site.

Acknowledgements

This work has been performed in the joint research project CryPhysConcept–Mit Kristallphysik zum Zukunftskonzept elektrochemischer Energiespeicher (03K3029A), which is financially supported by the Federal Ministry of Education and Research (BMBF). F.M. would especially like to thank Alexander Shevchenko for his fast and detailed help and answers with the programme StatPack and the work group in Samara for all discussions around ToposPro. W.M. acknowledges financial support from the Federal Ministry for the Environment, Nature Conservation, Building and Nuclear Safety within the joint-research project BaSta–Batterie Stationär in Sachsen (0325563D). N.A.K. and V.A.B. thank the Russian government (grant no. 14.B25.31.0005) and the Russian Ministry of Science and Education for support.

Keywords: crystal engineering • data mining • electrochemistry • intercalation • ionic conductivity

- [1] Z. Yang, J. Zhang, M. C. W. Kintner-Meyer, X. Lu, D. Choi, J. P. Lemmon, J. Liu, *Chem. Rev.* **2011**, *111*, 3577–3613.
- [2] X. Lu, G. Xia, J. P. Lemmon, Z. Yang, *J. Power Sources* **2010**, *195*, 2431–2442.
- [3] T. Nestler, R. Schmid, W. Münchgesang, V. Bazhenov, J. Schilm, T. Leising, D. C. Meyer, *ALP Conf. Proc.* **2014**, *1597*, 155–184.
- [4] V. A. Blatov, G. D. Ilyushin, O. A. Blatova, N. A. Anurova, A. K. Ivanov-Schits, L. N. Dem'yanets, *Acta Crystallogr. Sect. A* **2006**, *62*, 1010–1018.
- [5] N. A. Anurova, V. A. Blatov, G. D. Ilyushin, O. A. Blatova, A. K. Ivanov-Schitz, L. N. Dem'yanets, *Solid State Ionics* **2008**, *179*, 2248–2254.
- [6] J. Gao, G. Chu, M. He, S. Zhang, R. J. Xiao, H. Li, L. Q. Chen, *Sci. China Phys. Mech. Astron.* **2014**, *57*, 1526–1535.
- [7] S. Adams, R. Prasada, *Phys. Status Solidi A* **2011**, *208*, 1746–1753.
- [8] E. Levi, G. Gershinsky, D. Aurbach, O. Isnard, *Inorg. Chem.* **2009**, *48*, 8751–8758.
- [9] M. Ø. Filsø, M. J. Turner, G. V. Gibbs, S. Adams, M. A. Spackmann, B. B. Iversen, *Chem. Eur. J.* **2013**, *19*, 15535–15544.
- [10] V. A. Blatov, *Cryst. Res. Technol. Cryst. Rev.* **2004**, *10*, 249–318.
- [11] V. A. Blatov, A. P. Shevchenko, D. M. Proserpio, *Cryst. Growth Des.* **2014**, *14*, 3576–3586.
- [12] A. Belsky, M. Hellenbrandt, V. L. Karen, P. Luksch, *Acta Crystallogr. Sect. A* **2002**, *58*, 364–369.
- [13] M. S. Whittingham, *Chem. Rev.* **2004**, *104*, 4271–4301.
- [14] T. Kawaguchi, K. Fukuda, M. Oishi, T. Ichitsubo, J. Mizuki, E. Matsuura, *Acta Crystallogr. Sect. A* **2014**, *70*, C588.
- [15] M. S. Dresselhaus, G. Dresselhaus, *Adv. Phys.* **2002**, *51*, 1–186.
- [16] A. Van Der Ven, J. Bhattacharya, A. A. Belak, *Acc. Chem. Res.* **2013**, *46*, 1216–1225.
- [17] G. Hautier, A. Jain, S. Ping Ong, B. Kang, C. Moore, R. Doe, G. Ceder, *Chem. Mater.* **2011**, *23*, 3495–3508.
- [18] R. D. Shannon, C. T. Prewitt, *Acta Crystallogr. Sect. A* **1969**, *25*, 925–946.
- [19] R. A. Huggins in *Diffusion in Solids: Recent Developments* (Eds.: A. S. Nowick), Academic Press, **1975**, Chapter 9, "Very Rapid Transport in Solids", pp. 445–486.
- [20] *International Tables for Crystallography, Vol. A* (Ed.: T. Hahn), Wiley-VCH, **2005**.
- [21] Y.-F. Y. Yao, J. T. Kummer, *J. inorg. nucl. Chem.* **1967**, *29*, 2453–2466.
- [22] S. Komaba, N. Kumagai, R. Kumagai, N. Kumagai, H. Yashiro, *Solid State Ionics* **2002**, *152–153*, 319–326.
- [23] L. W. Shacklette, T. R. Jow, L. Townsend, *J. Electrochem. Soc.* **1988**, *135*, 2669–2674.

Received: May 20, 2015

Published online on September 23, 2015