Crystallochemical tools in the search for cathode materials of rechargeable Na-ion batteries and analysis of their transport properties

Stanislav S. Fedotov[a,b,*], Natalya A. Kabanova[c], Artem A. Kabanov[c], Vladislav A. Blatov[c,d],
Nellie R. Khasanova[a], Evgeny V. Antipov[a,**]

[a] Department of Chemistry, Lomonosov Moscow State University, 119991 Moscow, Russia
[b] Skolkovo Institute of Science and Technology, Skolkovo 143025, Moscow Region, Russia
[c] Samara Center for Theoretical Materials Science (SCTMS), Samara University, 443011 Samara, Russia
[d] School of Materials Science and Engineering, Northwestern Polytechnical University, Xi'an, Shaanxi 710072, People's Republic of China

ARTICLE INFO

ABSTRACT

In this work, we present a combined approach comprising of crystallochemical methods such as Voronoi-Dirichlet partition (VDP), bond valence sums mapping (BVSM) and bond valence energy landscapes (BVEL) for the search for Na-ion cathode materials. Using this approach a systematic screening of the inorganic crystal structure database (ICSD-2016/2) was performed to extract potential cathode materials for Na-ion batteries. As a result, a down-selected and reviewed list of known and newly discovered cathode materials compared and characterized structurally with a special focus on Na^+ mobility properties revealed by crystallochemical methods is given. DFT calculations were also carried out for a number of materials to validate the screening algorithm, applicability and reliability of the crystallochemical approaches as well as to get a deeper insight on the Na^+ diffusion properties.

1. Introduction

Crystal chemistry undoubtedly plays a crucial role in materials science [1–5]. Mostly, structure motifs and peculiarities determine a huge variety of functional properties of the material, with strong correlations between them being well established experimentally. At present > 600,000 entries of crystal structures of inorganic compounds are deposited in numerous databases. A substantial number of those compounds have already been turned into outstanding materials; some of them are still waiting for an opportunity. Manual screening of these databases is usually a complex and time-consuming process. Moreover, it is not insured against errors because some crucial candidates might be accidentally omitted or falsely neglected due to the so-called human element. That is why computer-assisted methods of screening (generally referred to as data-mining), which can provide accurate comprehensive analysis of huge and often uniform datasets as well as significantly cut time costs, set a growing trend [6,7]. In such cases, the dataset is filtered and processed according to the specific criteria, then sorted and analyzed automatically by specialized software. Generally, this procedure is iterated several times to exclude software bugs or computational errors. Finally, a down-selected set of prospective compounds requiring further manual examination is yielded. Thus, an initially immense array of structure data is narrowed down to a reasonable selection that can be easily manipulated and investigated.

This strategy can be extended to search for new candidate materials for various applications providing that their functional properties directly or indirectly arise from the crystal structure. The range of possible applications might span multiferroics, thermoelectrics, catalysts and energy storage materials including electrode materials for metal-ion batteries [8–11].

Recently, following the established trends in energy storage aimed at diminishing the net price of the rechargeable battery, a great number of new abundant and low-cost Na-ion electrode materials has been erupted by scientific community [12–14]. In most cases, the idea behind this or that material was based upon drawing analogy with existing and successful ones or taking into account heuristic chemical considerations. At the same time, targeted screening among existing compounds deposited in various structural databases could also be an efficient tool to elucidate new ideas and give hints on the design of novel Na-ion electrode materials.

Crystallochemical approaches such as geometrical (Voronoi-Dirichlet partition, VDP) [15] and bond valence (BV) methods [16]

---

have already shown efficiency in assessment or search for metal-ion electrode materials [17–19] or solid ionic conductors [20–22]. These approaches certainly score over much complicated ab-initio calculations in terms of time-consumption and price. However, each of them possesses its own intrinsic limitations, which could be partly removed when the approaches are applied together thus enhancing accuracy of the obtained data. In this work, we propose a combined crystallochemical approach comprising of VDP and BV methods (bond valence maps and bond energy landscapes [23]) for a systematic screening of the inorganic crystal structure database (ICSD-2016/2) to extract potential compounds, which can be regarded as cathode materials for Na-ion batteries. As a result, we present a down-selected and thoroughly reviewed list of known and newly discovered cathode materials compared and characterized structurally with a special focus on Na^+ mobility properties revealed by crystallochemical approaches. The latter group of materials is anticipated to deliver quite attractive electrochemical performance. DFT calculations were also carried out to validate the screening algorithm and applicability of the crystallochemical approaches as well as to get a deeper insight on Na^+ diffusion properties. The goal of this paper is also to testify high reliability and predictive abilities of the crystallochemical approaches that is affirmed by a substantial set of direct experimental evidences.

1.1. Terminology and theoretical aspects

1.1.1. Direct geometry approach: Voronoi-Dirichlet partition (VDP)

Cation conductive properties of inorganic crystalline solids are largely determined by the existence of a continuous system of channels available for the cation migration. According to the Voronoi-Dirichlet partition approach, the crystal space is represented as two dual subspaces: atoms and voids [24]. To investigate cation migration paths using this approach Voronoi-Dirichlet polyhedra (VDP) are built only for so-called "framework" atoms, which do not participate in the ion transport. The vertices and edges of VDP correspond to the elementary voids and channels (Fig. 1, A). The set of VDP vertices and edges form a periodic graph, which corresponds to the migration map of mobile cations that migrate through the system of voids and channels (Fig. 1, B). Generally, the voids and channels are characterized by their radii R_{sd}, and Rad parameters, respectively [24]. The procedures for constructing the graph and polyhedral representations of the void space as well as the subsequent analysis of their geometrical-topological characteristics are implemented in the program package ToposPro [25].

Not all elementary voids and elementary channels are suitable for the mobile cations, but only significant ones, which have sufficiently large R_{sd}, and Rad radii [24]. The migration map for LiFePO$_4$ is shown in Fig. 1, B. The VDP method results in zig-zag shaped 1D pathways, which are now verified by a number of much more sophisticated computational and even experimental techniques.

1.1.2. Bond valence methods

Originally, the "bond valence" (BV) idea derives from Pauling's "bond strength" rule, with interatomic distances being taken into account. When summed around the anions and cations, the bond valences were found to reproduce accurately the atomic valences (formal ionic charges).The bond valence sum (BVS) of an atom can be calculated according the following formula:

$$BVS = \sum_{j=1}^{N} \left[\exp\left(\frac{R_o - d_j}{b} \right) \right], \tag{1}$$

where d_j is the bond length, R_0 and b are tabulated constants.

Since that, the concept of bond valence summation has been extensively developed. Now the idea is widely recognized as a method of locating the positions of light elements in the presence of heavy ones and as a simple tool of validating crystal structures. Lately, some new applications emerged in the field of ionic conductors [26]. In this field,
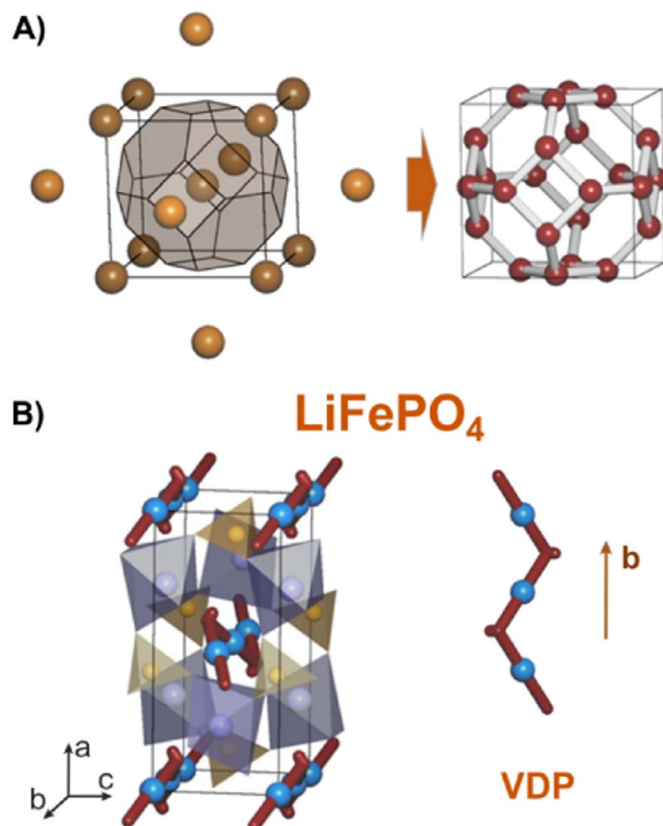

Fig. 1. A) VDP constructed for a central atom in a body-centered cell (left). A set of vertices and edges of VDP with voids centers being designated as brown spheres and migration channels as grey cylinders (right). B) A migration map represented as a graph of significant voids and channels for LiFePO$_4$ (left) and one of the zig-zag shaped 1D migration pathways (right). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

a construction of bond valence maps is used to define and directly visualize mobile ion diffusion pathways within the crystal structure. For this purpose, a unit cell is partitioned with a given step (usually, 0.2 Å). Then in each section, a BVS value is automatically calculated for a testing ion (within the scope of this work the testing ion is Na^+) and finally three-dimensional map is recorded. A key characteristic of this map is a so-called BVS cutoff (or mismatch) value. This parameter limits the deviation of BVS from the reference value (1 for Na). The more the deviation in a particular area, the lower possibility for Na^+ to move through this area. Normally, a reasonable deviation of mismatch values for a mobile ion should not exceed 10–15% of its reference value (or formal oxidation state). This approach can be performed with bond valence sums mapping (BVSM) script implemented in 3DBVSMAPPER program 27]. Fig. 2A contains an example of a BVS map created for LiFePO$_4$. It should be noted that Formula (1) does not consider Coulomb repulsion. Therefore while operating 3DBVSMAPPER generates blocking spheres around atoms with the same sign of oxidation state as Na^+ to avoid building unphysical landscapes.

The chemical plausibility of BVS mismatch calculations can be enhanced by addition of penalty functions to take into account sites with highly asymmetric coordination and exclude those close to other similarly charged ions via Coulomb repulsions. Obviously, a high BV mismatch should imply a high site energy, $E(A)$, that can be estimated according to the following link formula [28]:

$$E(A) = D_0 \left| \sum_X s_{A-X} - V_{id}(A) \right|^g + E_{asym} + E_{rep}, \tag{2}$$

where E_{asym} represents an energy penalty due to the asymmetry of the