The theoretical evaluation of new promising solid ion conductors for zinc-ion batteries

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Abstract. Recently, we have screened the Inorganic Crystal Structure Database (ICSD, version 2020/1) to find new Zn$^{2+}$-ion conductors. After a stepwise selection procedure, we have identified five most promising Zn-ion conductors ZnFe$_2$O$_4$, ZnV$_2$O$_4$, ZnCr$_2$O$_4$, ZnP$_2$O$_6$ and Zn$_3$S$_2$O$_9$. In this work we describe the ion conductivity in the selected structures in detail by using of a set of methods: analysis of free space in crystals (geometrical-topological analysis, based on the Voronoi partitioning approach), calculation of the Zn$^{2+}$-ion migration energy barrier within the bond valence site energy method, and calculation of the Zn$^{2+}$-ion energy barriers within the density functional theory approach.

1. Introduction
The current trend in battery materials science is in the searching of most prospective post-lithium batteries. This is caused by depletion of lithium natural sources as well as ecological and political issues [1]. In this regard, the urgent task of materials science is the search for new compounds with high ionic conductivity, which can be used as components for multivalent or high-valent metal-ion batteries, fuel cells or gas sensors [2]. Such materials with high ionic and low electronic conductivity are generally called solid electrolytes (SE).

Traditionally, alkali metal-ion batteries (Na$^+$, K$^+$) are considered as most viable alternative to the lithium ones. However, high-valent metal-ion batteries also look very promising due to the availability and low cost of raw materials and higher charge of the working ions [1]. Here we report on the evaluation of Zn-ion conductivity in the most prospective compounds, which were selected as a results of a step-by-step theoretical searching of ion conductors among ternary and quaternary oxygen-containing compounds for prospective Zn-ion batteries (ZIB).

Among the most promising advantages of Zn-ion batteries there are – three times higher theoretical capacity and low price compared to lithium-ion batteries (LIB). Theoretically, the aluminium-ion batteries have even better characteristics than Zn-ion ones (Figure1), though the search of materials with aluminium-ion conductivity is challenging [3].
Zn-ion batteries have another positive aspect: higher safety and reduced environmental impact. These are reasons for the growing interest in ZIB during the last years [4].

The search for promising Zn-ion SE was performed using high-throughput screening of crystal structure data from the ICSD (version 2020/2) based on geometrical-topological (GT) analysis, fast semi-quantitative bond valence site energy (BVSE) modelling, determination of ionic conductivity by using the kinetic Monte Carlo (KMC) method and quantum-chemical simulation of ion transport within the Density Functional Theory (DFT). The overall process and the combined and stepwise applied methods are described in [5] in detail. This approach is rather universal and was successfully used for searching of monovalent [6–8] and multivalent metal-ion conductors [9].

The combination of four aforementioned methods allows for making accurate theoretical selections of SE with possible practical application, which significantly reduces the searching time and resource consumption for the synthesis. Thus, we found five most promising potential Zn-ion conductors, three of which can serve as cathode materials for ZIB.

2. Methods

2.1. Geometrical-topological approach

The first step of combined investigation is the GT approach, which is implemented in the ToposPro program package [10] and based on the Voronoi partition model of the conducting framework [11]. The obtained Voronoi polyhedra fill the crystal space. Further, analysis of the free space is carried out for the presence of wide voids and connected channels available for zinc migration by using the geometrical parameters.

Threshold values of geometrical parameters were determined by comparing theoretically calculated migration maps with experimental data. Those values were chosen when migration maps are generated for each known cationic conductor. We applied these criteria and found significant voids and connecting channels that are available for zinc migration. If the migration map is infinite in at least one direction, i.e. it has a dimension of 1, 2 or 3, then the structure may be a possible ionic conductor.

We should note that similar GT analyses were already successfully applied by the authors for the searching of new alkali metal-ion conductors [7, 8, 9] and high-valent ion conductors [3, 9]. These data, coupled with gathered literature data, were organized in form of a public database with both known and theoretically predicted ternary and quaternary ion conductors with a wide set of working ions: Li$^+$, Na$^+$, K$^+$, Ag$^+$, Mg$^{2+}$, Ca$^{2+}$, Sr$^{2+}$, Zn$^{2+}$, Al$^{3+}$. The database is currently available in the Internet at http://batterymaterials.info and constantly updated by the authors.

2.2. BVSE simulations

The semi-quantitative evaluation of the Zn$^{2+}$-migration energy barriers was carried out by the BVSE method. Chen et al. [12] implemented the β-GUI version of the softBV program for BVSE-calculation. If the deviation of the values from the bond valence sum (BVS) for an ion in a specific region of the structure does not exceed 10%–15%, then the probability of finding this ion in this crystallographic space is high.

We calculated the migration energies for each ion species in the structure to exclude those with cationic conductivity. This method does not take into account the Coulomb repulsion of the
framework ions that do not participate in migration but gives a quick preliminary quantitative estimate of the ion transport. Next, we calculated the ionic mobility at room temperature by using KMC simulations. The KMC algorithm – as implemented in softBV [12] – uses the approximate site energies and barrier heights as obtained from the BVSE analysis.

2.3. DFT-calculation

The migration energies of working ions ($E_m$) were calculated within the DFT approach [13-14] using the VASP package [15]. The $E_m$ values were obtained using the Nudged Elastic Band (NEB) method as it is implemented in the VASP package. The input data for the NEB calculations were prepared with the assistance of the PATHFINDER script (http://batterymaterials.info/downloads).

The activation energy $E_a$ of ionic conductivity consists of two components: the migration energy $E_m$ and the vacancy formation energy $E_v$: $E_a = E_m + E_v$ [16]. The standard formula (1) for estimation of the vacancy formation energy $E_v$ for oxygen sites was used:

$$E_v(Zn) = E_{\text{defect}} + E_{Zn} - E_{\text{bulk}},$$

where $E_{\text{bulk}}$ and $E_{\text{defect}}$ are the total energies of the bulk structure and the structure with an introduced vacancy (one neutral Zn per original unit cell was removed), while $E_{Zn}$ represents the total energy of a Zn atom in the bulk metal.

3. Results and discussions

We found 782 Zn-containing inorganic compounds in the ICSD, in which the anionic framework is formed solely by oxygen atoms. After GT analysis, 334 compounds with 1D, 2D or 3D Zn$^{2+}$-ion migration map were selected, 83 of which are unknown as possible Zn$^{2+}$ ion conductors before.

BVSE-calculations were performed for the 83 compounds and for each atomic species in the structure to exclude a preferred conductivity of other ions. Thus, we found 27 Zn$^{2+}$-ion conductors with low migration energies ($E_m < 0.8$ eV).

![Figure 2. 3D Zn$^{2+}$ migration maps for Zn$_3$S$_2$O$_8^-$, Zn$_3$P$_2$O$_6^-$ (top panels a and b); 3D Zn$^{2+}$ migration maps (bottom left panel c) and corresponding migration energy profiles for ZnM$_2$O$_4$ (M=V, Cr, Fe) from BVSE-modeling.](image-url)
For further processing we selected those compounds with 2D and 3D migration maps since there are advantageous for application in polycrystalline form.

Finally, we selected 20 compounds for KMC simulation. Among them, 4 compounds (Zn$_2$P$_2$O$_6$, ZnFe$_2$O$_4$, ZnCr$_2$O$_4$, ZnV$_2$O$_4$) with high ionic conductivities above $10^{-6}$ S/cm and low migration energies ($E_m < 0.7$ eV) were selected for DFT-modelling. Zn$_3$S$_2$O$_9$ was also chosen because it consists of readily available elements and its parameters are comparable (see Table 1). Figure 2 presents Zn$^{2+}$ migration energies and energy isosurfaces, which indicates migration maps, for five most interesting SE: Zn$_3$S$_2$O$_9$, Zn$_2$P$_2$O$_6$ and spinel-like ZnM$_2$O$_4$ (M=V, Cr, Fe) according to BVSE-modeling.

Table 1 summarizes the main parameters of the five selected compounds (Zn$_3$S$_2$O$_9$, Zn$_2$P$_2$O$_6$ and ZnM$_2$O$_4$ (M=V, Cr, Fe)).

| Migration map from GT | $\sigma_{tr}$ (S/cm) | $E_m$ (eV) (BVSE) | $\Delta E_m$ (eV) | $E_m$ (eV) (DFT) | $E_v$ (eV) | $C_g$ (mAh/g) | $C_v$ (mAh/cm$^3$) | $E_g$ (eV) |
|---------------------|----------------------|--------------------|------------------|------------------|----------|-------------|----------------|-----------|
| ZnP$_2$O$_6$        | 2D                   | $4 \times 10^{-6}$ | 0.69             | 0.77             | 0.68      | 7.05        | -              | -         | 4.716       |
| Zn$_3$S$_2$O$_9$    | 3D                   | $3 \times 10^{-5}$ | 0.80             | 1.06             | 1.55      | 5.35        | 222            | 1142      | 1.694       |
| ZnFe$_2$O$_4$       | 3D                   | $5 \times 10^{-5}$ | 0.44             | 0.49             | 0.54      | 0.46        | 345            | 1755      | 0.000       |
| ZnV$_2$O$_4$        | 3D                   | $<2 \times 10^{-5}$| 0.36             | 0.61             | 0.55      | 1.01        | 348            | 1700      | 2.623       |
| ZnCr$_2$O$_4$       | 3D                   | $6 \times 10^{-5}$ | 0.36             | 0.66             | 0.70      | 1.95        | 348            | 1700      | 2.623       |

According to the DFT calculations, the spinel-like structures ZnM$_2$O$_4$ (M=V, Cr, Fe) have the lowest Zn-ion migration barriers ~0.6 eV/ion – 0.7 eV/ion (see Figure 3). Among them, ZnV$_2$O$_4$ has a zero band gap energy according to the https://materialsproject.org database and is therefore possibly most suitable as active cathode material.

![Figure 3. Calculated Zn$^{2+}$ ion migration map (left panel) and corresponding migration energy profiles for spinel-like ZnM$_2$O$_4$ (M=V, Cr, Fe) structures using the DFT approach.](image)

Zn$_3$S$_2$O$_9$ and ZnP$_2$O$_6$ compounds have a band gap energy $>3$eV and no redox-active transition metal, so they can be characterized as promising solid electrolytes for all-solid-state ZIBs. Migration energy profiles for Zn$_3$S$_2$O$_9$ and ZnP$_2$O$_6$ from DFT calculations are shown in Figure 4a and Figure 4b, respectively.

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Figure 4. Calculated Zn$^{2+}$ ion migration map (top left panel) and corresponding migration energy profiles (top right panel) for Zn$_3$S$_2$O$_9$ and calculated Zn$^{2+}$ ion migration map (bottom left panel) and corresponding migration energy profiles (bottom right panel) for ZnP$_2$O$_6$ using the DFT approach.

We propose some variants of a Zn-ion all-solid-state battery considering the determined parameters, as it is shown in Table 2. ZnP$_2$O$_6$ and Zn$_3$S$_2$O$_9$ consist of readily available elements, have the higher $\sigma_{RT}$ and can be considered as solid electrolytes. As cathode, we suggest ZnFe$_2$O$_4$, ZnCr$_2$O$_4$ or ZnV$_2$O$_4$ because they all have comparably high ionic conductivities and volumetric capacities. Such variants could be interesting for practical application.

Table 2. The components of a potentially outstanding Zn-ion all-solid-state battery.

| Characteristics | (-) Anode | Solid electrolyte | Cathode (+) |
|-----------------|-----------|-------------------|-------------|
| $C_v$, mAh/cm$^3$ | Zn | ZnP$_2$O$_6$ | Zn$_3$S$_2$O$_9$ | ZnFe$_2$O$_4$ | ZnCr$_2$O$_4$ | ZnV$_2$O$_4$ |
| $\sigma_{RT}$, S/cm$^{-1}$ | - | $4 \times 10^{-6}$ | $3 \times 10^{-5}$ | $2 \times 10^{-5}$ | $6 \times 10^{-5}$ | $2 \times 10^{-5}$ |

4. Conclusion

The step-by-step high-throughput computational searching for ternary and quaternary zinc oxides with periodic Zn$^{2+}$ migration maps resulted in five most promising compounds: ZnP$_2$O$_6$, Zn$_3$S$_2$O$_9$, ZnFe$_2$O$_4$, ZnV$_2$O$_4$, ZnCr$_2$O$_4$, which are meant to be prospective solid electrolytes and cathode materials for a potential Zn-ion all-solid-state battery. At the moment we are synthesizing these structures for further experimental verification.

5. References

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