

Combined crystallochemical and quantum-chemical search for new high-valent chalcogen-containing ionic conductors

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Improvement of existing batteries is a hot topic due to both the rapid spread of mobile technologies and the impetuous growth of the electric vehicle sector. The commonly used lithium-ion batteries (LIB) have a number of well-known disadvantages: flammability and high lithium price due to limited natural resources. The moderate capacity of LIBs is a further challenge for high-performance mobile devices. Theoretically, all-solid-state batteries based on high-valent working ions, such as magnesium, zinc or aluminum, can have higher volumetric capacities compared to LIBs [1].

We report the results of the high-throughput search for new solid electrolytes (SE) and cathode materials for high-valent metal-ion batteries. We focused on Mg-, Ca-, Zn- and Al-containing ternary and quaternary chalcogenides. Theoretically, S-, Se- or Te-containing compounds should exhibit higher cation conductivities than their oxygen analogues. It can be explained by a lower degree of ionicity in chalcogenides in comparison to oxides [2]. Our study was performed by using a well-established high-throughput screening algorithm [3]. The algorithm consists of three main steps: (a) fast topological-geometrical screening; (b) bond valence site energy (BVSE) modeling for a preliminary quantitative estimation and (c) precise quantum-chemical modeling of ionic transport.

All ternary and quaternary Mg, Ca, Zn and Al chalcogenides (1572 structures) were extracted from the ICSD (version 2020/1). Among them, a group of promising cation conductors with 1D-, 2D-, or 3D-migration maps was identified by using the Voronoi partitioning algorithm as implemented in the ToposPro package [4]. We obtained 72 S-, 30 Se- and 11 Te-containing high-valent ion conductors. The BVSE method was utilized for determination of migration energies of all species in the compounds, and a group of most promising compounds with migration barriers $E_m \leq 0.5$ eV and the difference in the migration energies with other ions $\Delta E_m \geq 0.5$ eV was selected. This group includes, in particular, MgLu_2Se_4 , MgHo_2Se_4 , $\text{ZnLa}_3\text{GaSe}_7$, $\text{Al}_{5,9}\text{SnTe}_{9,892}$, $\text{Al}_2\text{Be}_2\text{La}_6\text{S}_{14}$, $\text{Al}_{3,3}\text{Dy}_6\text{S}_{14}$, $\text{Al}_{3,3}\text{La}_6\text{S}_{14}$ compounds. In a final step, the density functional theory (DFT) modeling was carried out for the structures with lowest E_m compounds. The Nudged Elastic Band (NEB) method was used as implemented in the VASP package [5]. Figure 1 shows a good agreement of migration maps between the three applied approaches.

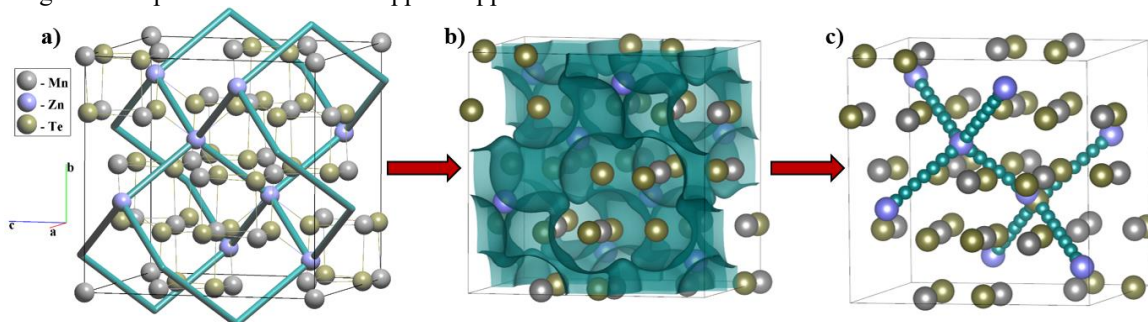


Figure 1. 3D Zn^{2+} -migration map for ZnMn_2Te_4 compound in terms of crystallochemical analysis (a), bond valence site energies (b) and quantum-chemical modeling (c).

All results were uploaded to the web site <http://batteryaterials.info>, where they are available free of charge.

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