Computational search for novel Zn-ion conductors—a crystallochemical, bond valence, and density functional study

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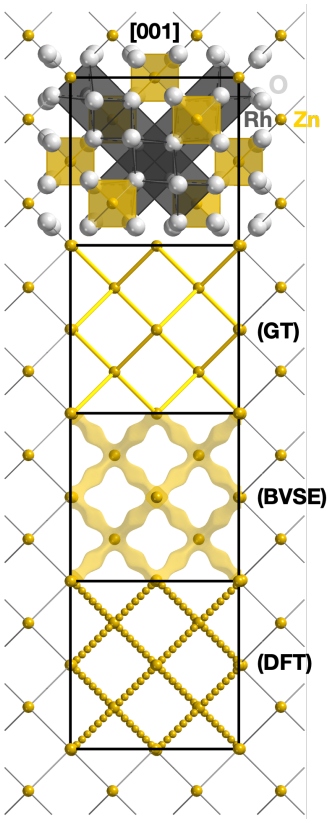
Zinc-based batteries have been a recurring theme throughout history, from Volta's pile, the Daniell and Leclanché elements to powering modern space vehicles. To date, no rechargeable all solid-state Zn-ion battery has been commercialized. Therefore, we intended to contribute to increasing the number of available Zn^{2+}-ion conductors for such batteries.



We used a stepwise algorithm [1, 2] to identify compounds from the ICSD prone to Zn^{2+}-ion conductivity; the figure shows the example of $ZnRh_2O_4$. The rapid geometrical–topological (GT) screening based on Voronoi partition was utilized as the first step. 334 of 782 Zn-/O-containing compounds that possess Zn^{2+} migration maps have been found. Among them, 83 compounds were previously unknown as possible Zn^{2+} conductors. Then we applied bond valence site energy (BVSE) calculations to evaluate migration energies for the Zn^{2+} conduction. Of the 83 compounds, 27 fulfilled the condition of being solely Zn^{2+} conductors. For the most promising compounds, we used the Nudged Elastic Band (NEB) method within the density functional theory (DFT) approach to verify Zn^{2+} conductivity.

Most interesting compounds are ZnM_2O_4 (M = Fe, Cr, V) and ZnP_2O_6 with migration energies of less than 0.7 eV/ion. Finally, we simulated ionic conductivities within the kinetic Monte Carlo approach yielding values of up to 10^{-3} S/cm. We further studied the *complexity* of the promising structures. The data was uploaded to our database batterymaterials.info.

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[2] Ye. A. Morkhova, M. Rothenberger, T. Leisegang, S. Adams, V. A. Blatov, A. A. Kabanov: Computational search for novel Zn-ion conductors–a crystallochemical, bond valence, and density functional study. *J. Phys. Chem. C* 125, 17590–17599 (2021).

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