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HIGH-THROUGHPUT AB-INITIO CALCULATIONS: MATERIALS FOR ENERGY STORAGE

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At present time, sodium-based batteries are considered as the most viable candidates for replacing widespread lithium batteries. Al- and K-based materials (among others) are also envisaged as prospective compounds for the next generation of solid state batteries (SSB). We are calculated the possible migration pathways for a number of Na-, Al-,K- and Li-conductive materials and selected new perspective compounds from ICSD database using ToposPro package, specially designed for study of super-ionic conductors. For the most promising compounds a careful analysis using DFT calculations was performed. The combined study with both topological and DFT approaches is crucial to gain insight into the main features of ionic conductivity.

Keywords: materials science, solid-state battery, ab-initio method, DFT.

Introduction

The existing technologies demands to portable energy sources. Such sources should be safe, cheap, effective, compact and environment-friendly. During past two decades lithium-ion batteries provides impressive advances in mobile electronics and electric vehicles [1,2]. This technology's jump was possible due to remarkable properties of lithium-conductive materials, especially high energy density. At the same time, the researchers have been exploring a lot of new materials for energy-storage applications and a routes to increase solid-state battery performance (specific energy, cyclability etc.) [3-8]. From the other side, battery safety stay a cornerstone for designing of new materials (remember the recent battery fires on commercial Boeing airplanes in 2013-2014). One more reason affected on the searching is the lack of lithium for large-scale applications (for example, grid-based energy storage system for renewable energy sources) [9]. This lead to active exploring of sodium, potassium, aluminium-conducting materials as promising candidates for replace Li-conducting ones.

The modern computational methods provide an excellent opportunity for numerical investigation of materials. Density functional theory – based methods (also called as first-principles, or ab-initio methods) able to predict a key properties of materials, including ion mobility, electronic structure, cell voltage, thermal stability and voltage profiles [10]. DFT-based calculations open so called «high-throughput» searching then a lot of materials are explored computationally without time- and resource-consuming experiments.

Here we present recent results of DFT calculations of different types of ion-conductive materials using Vienna ab-initio Simulation Package (VASP) [11]. All calculations were performed using general gradient approximation GGA (or GGA+U, depending of material's chemical composition) approximation. Also ToposPro [12] geometrical tiling analysis was used to predict non-equivalent elementary migration channels in the structures. The combination of topo-

logical and quantum-mechanical investigations allow to achieve the most comprehensive results.

Results

The following compounds were investigated using combined topological and DFT-based approaches: LiCoO2 [13], Li2CoPO4F, LiVPO4F, KFeO2, NaFePO4, NaMnAsO4, NaFeVF7, Al2(WO4)3, AlFe2O4 and some others. The migration maps, activation energy barriers and electronic band were computed. Usually structures have a few possible migration pathways and we calculated the activation energies for each of them. The obtained results are summarized at Table 1 (if the compound has a few migration pathways activation energies for each path separated by semicolon).

Table 1. The activation energy barriers for selected compound. Bold elements are migrate during diffusion

Compound	Activation energy barrier(s), eV/ion
Li**CoO$_2$**	**0.52**
Li$_2$**CoPO$_4$F**	**0.1; 0.58; 0.49; 0.25**
Li**VPO$_4$F**	**0.72**
K**FeO$_2$**	**0.13; 0.24; 0.29; 0.32; 0.49**
Na**FePO4**	**0.25, 2.51**
Na**MnAsO$_4$**	**0.42, 2.59**
Na**FeVF$_7$**	**1.13**
Al$_2$**(WO$_4$)$_3$**	**2.69**
Al**Fe$_2$O$_4$**	**0.74**
Al**VO$_4$**	**1.14**

An examples of electronic band structures of the compounds are presented at Figs. 1-2.

Based on our results (Table 1) we can suppose that $KFeO_2$, Li_2CoPO_4F and, possibly, NaFePO4 has a good parameters for ionic conductivity. Due to its electronic band gap Li_2CoPO_4F can be used as solid electrolyte in SSB.

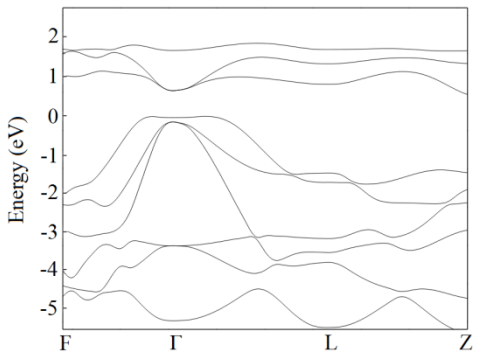

Fig. 1. Band structure of $LiCoO_2$ in the primitive unit cell

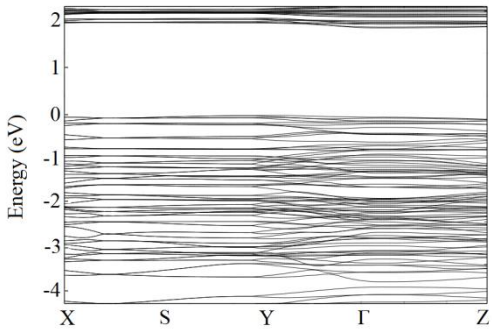

Fig. 2. Band structure of Li_2CoPO_4F in the primitive unit cell

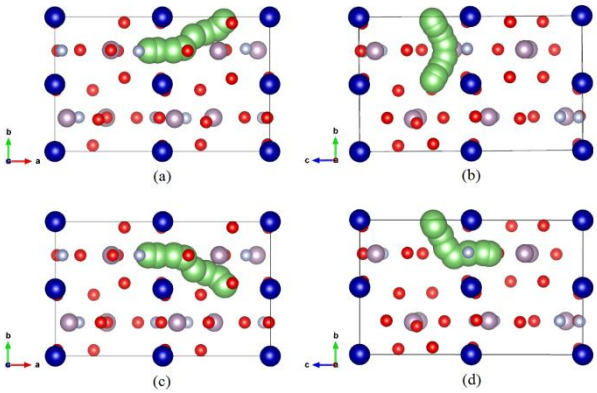

Fig. 3. The migration pathways of Li_2CoPO_4F in the primitive unit cell

Summary

In this work we performed high-throughput searching of materials for energy storage. We proposed a few prospective compounds which can be useful for future solid-state batteries. Topological and quantum-mechanical approaches (using ToposPro and VASP) for theoretical analysis of ionic conductivity were employed.

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