MODERN APPROACHES TO CALCULATION OF THE PROPERTIES OF MATERIALS FOR ENERGY STORAGE

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The modern technologies demands to compact and effective rechargeable systems of energy storage. Such systems needs for electronic devices, spacecrafts, hybrid cars etc. At the present time the Li-ion based batteries are among most popular rechargeable systems for different devices. Actual task in this area is searching of new perspective materials for cathodes, anodes and solid electrolytes. The goal of this task is creation Li-batteries with improved parameters such as capacity, energy density, cyclability. But the use Li-batteries for long-term and large-scale applications face some critical concerns, such as limited lithium resources and their increasing price. And here arises another task - searching of materials for the other type batteries (Na, K, etc.). Computational methods is very attractive to solving both mentioned tasks: modern computing packages allows to investigate the properties of a lot of hypotetical compounds without experimental work. In this work we present the results of modelling of conducting properties of some perspective compounds for batteries.

Introduction

Research and development of rechargeable batteries having extremely high energy densities is one of the most important issues of the present science and technologies. To create these batteries need to find new materials with appropriate properties.

Now the most commonly used method for prediction of materials properties is Density Functional Theory (DFT) and packages, based on this theory – VASP [1], Wien2k [2], Quantum Espresso [3] etc. Additionally, migration map can be constructed from geometrical point of view – using ToposPro package [4], for example. Geometrical approach is very helpful to complex analysis of the structure and to construction the full migration maps.

In this work we investigated the activation energies of one promising compound – Li_2CoPO_4F using combination of two methods – ab-initio and geometrical calculations.

Computational methods

First-principles calculations are performed using DFT framework as implemented in the Vienna Ab-initio Simulation Package (VASP). The electron-ion interaction is described using a projector augmented wave method (PAW) using Perdew-Burke-Ernzerhof (PBE) pseudopotentials. After the corresponding accuracy tests, a kinetic-energy cutoff for valence electron wave functions is set to be 800 eV. The structure optimization is carried out using conjugate-gradient algorithm until the forces on each atom are less than 0.01 eV/A and the total energy is converged up to 10^{-6} eV. The nudged elastic band (NEB) method is adopted to find the kinetic energy barrier along diffusion pathways.

Results and discussion

The Li_2CoPO_4F can exist in two different forms – oxidyzed and non-oxidyzed. The lattice parameters after optimization for non-oxidyzed form are equal 10.158A, 6.323A, 10.540A for a,b and c direction respectively. For oxidyzed form lattice parameters are equal to 10.341A, 6.292A, 10.663A for a,b and c direction respectively. The obtained migration pathways for Li_2CoPO_4F are shown on Fig.1 and the corresponding activation energy barriers – on Fig.2. It is interesting that pathway 2 (migration in b-c plane) has extremely low values of energy barrier – only 0.08 eV (see Table 1). The other pathways also has quite low barriers. This result indicate that Li_2CoPO_4F can be very promising cathode material.

Table 1. The values of activation energy barriers for both form of Li_2CoPO_4F.

Path number	Activation energy for non-oxidized form, eV	Activation energy for oxidized form, eV
Path 1	0.41	0.47
Path 2	0.08	0.08
Path 3	0.49	0.44
Path 4	0.46	0.40

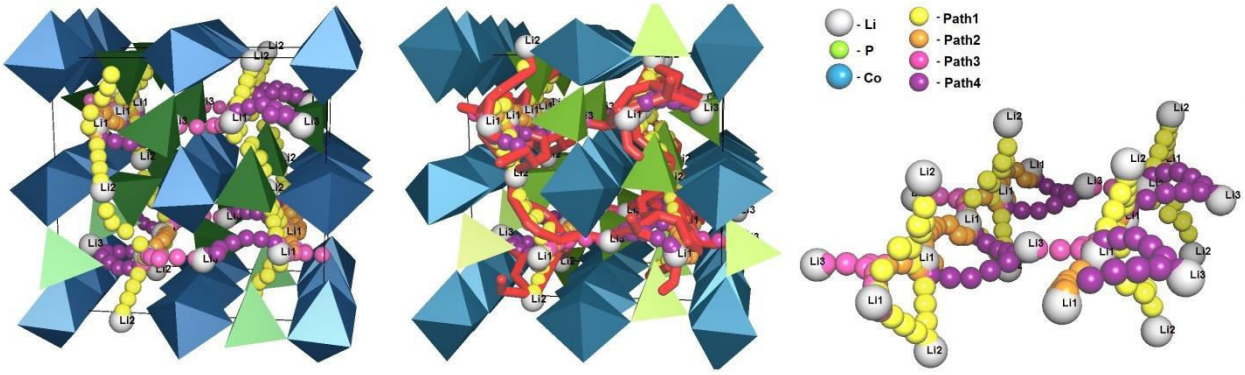

Figure 1. The structure and Li-ion migration pathways in Li_2CoPO_4F compound. (a) The structure of in Li_2CoPO_4F and the migration channels (marked by colored balls) obtained by NEB method; (b) The comparison between NEB-obtained pathways (colored balls) and geometrical pathways (red pipes); (c) The net of migrational channels.

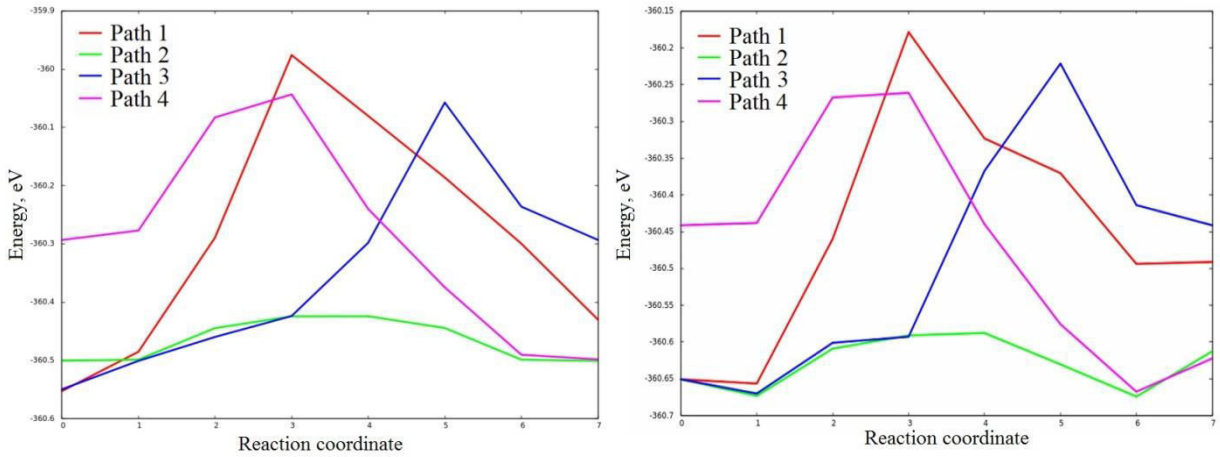

Figure 2. Activation energy barriers for Li_2CoPO_4F. Non-oxidyzed form are shown on the right, oxidized form – on the left.

References

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