PATHFINDER toolkit for analysis of ion migration pathways in solids

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Abstract. We have developed a set of shell scripts for an efficient generation and analysis of ion conductivity pathways in solids. This set of shell-scripts is called "PATHFINDER" and can be freely download at http://batterymaterials.info/downloads. PATHFINDER toolkit allows to identify ion migration pathways and generates corresponding structural files with pathways. PATHFINDER may help with transition state finding and subsequent precise DFT modeling (within NEB approach). We have shown a few examples how to apply scripts of searching for multivalent ion conductivity in magnesium-, calcium-, and strontium–oxygen-containing compounds.

1. Introduction

Searching for new solid ionic conductors became one of the most urgent task in material science over the last decade. This can be explained by ongoing growing of battery market due to enormous spreading of mobile technologies [1]. Lithium ion batteries (LIB) revolutionized existing technologies but the amount of lithium in the earth crust is very limited which leads to high cost of LIB. Post lithium ion batteries should be less expensive as well as much safe and environmentally friendly [2]. New materials with high ionic conductivity are needed for production of such batteries. Theoretical modeling provides an efficient way for searching of materials with desirable properties. Particularly, Density Functional Theory (DFT) [3-4] is one of the most powerful and commonly used approach in the field. Nudged Elastic Band method [5], which is implemented within numerous DFT packages the most popular instrument for quantitative theoretical assessment of ionic conductivity in solids. This method requires preliminary preparation of input structural files with diffusion trajectory of working ion. Here we present the PATHFINDER toolkit – a set of shell scripts for automatic analysis of possible diffusion pathways in solids. Presently this toolkit generate input files only for the VASP package [6] but we plan to extend it in the future for another popular DFT packages.

2. PATHFINDER toolkit: installation, basic functionality and settings

No specific installation procedure is needed. After extracting all files from archive, run *install* script in sudo mode.

PATHFINDER toolkit consists of two main shell scripts – PATHFINDER and ANALYTIC. PATHFINDER script determines the possible ionic conductivity pathways and generates necessary files for the DFT-NEB calculations (for the VASP package only, still). ANALYTIC script extracts the data after DFT-NEB calculations and summarise results.

The only input data to start searching of ionic diffusion pathways is structural file in the form of commonly used .cif file or VASP-specific POSCAR/CONTCAR format. Presently the searching procedure based on analysis of distances between nearest neighbours and the crystallographic

symmetry of atomic positions. The electronic density, which is an important factor for determination of ionic pathways, will be included in the next versions of the script.

Figure 1. The block of main parameters in the PATHFINDER script.

Inside the PATHFINDER script in the beginning, there are few settings, which users can change (Figure 1). Most important parameter is PATH_LENGTH, which is threshold value for searching of diffusion pathways. Any pathways which lenght is higher that PATH_LENGTH value will be excluded from further analysis. Other parameters concern precision and amount of intermediate images for the NEB calculations.

To start script you should use the following command in terminal:

./PATHFINDER $atomic_specie

Here $atomic_specie is the type of working ions for whom you would performs analysis. For example, the command «./PATHFINDER Li» will run searching of lithium diffusion pathways. The standard output of the PATHFINDER script is shown at the Figure 2. Also all output data will be recorded in the file PATHS.txt.
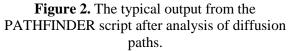
For the following DFT-NEB calculation, PATHFINDER creates enumerated directories like «PATH_N», where N is the number of pathway. Inside the directories you may find file PATH.vasp, which contains the initial trajectory of diffusion.

To remove all PATHFINDER's output files you may use the following command:

./PATHFINDER clear

The second script is ANALYTIC, which summarise results after DFT calculations. ANALYTIC provides the convenient way to analyse the data, including the migration barriers E_M and vacancy formation energies E_V. The following formula is used to estimate E_V:

Figure 2. The typical output from the PATHFINDER script after analysis of diffusion paths.

$$E_V(A) = E_{defect} + E_A - E_{bulk}. \qquad (1)$$

Here E_{bulk} and E_{defect} are the total energies of the bulk structure and the structure with an introduced vacancy. E_A represents the total energy of one $atomic_specie atom in the bulk. An example of the ANALYTIC output is shown at the Figure 3.

3. Conclusion
We have presented the first version of PATHFINDER toolkit for automatic searching and analysis of ion diffusion pathways in solids. The set of scripts is designed to be run by the Unix shell. Currently, the PATHFINDER support only the VASP calculations. Only the geometrical and crystallographic

approaches are used within the script. For the future we plan include electronic density analysis into the scripts and support more DFT codes.

```
Created by ANALYTIC script v.1.3.0.        Contact email: artkabanov@mail.ru
Date: 2019-12-26
-----------------------------------------------------------------------------
Bulk energy E(b):  -1256.22552651 (eV)
Energy E(specie):  -1.68333 (eV/atom)  |  E_vac_f = E(b) - (E + E(specie))

Path    E1           E2          E1-E2    Length   Em       E1_vac_f  E2_vac_f  E_ABOVE_NULL
-----------------------------------------------------------------------------
1    -1250.21960   -1250.21960   0.00000  3.57447  2.18400  4.32260   4.32260   0.00
2    -1250.21959   -1250.21960   0.00000  3.45580  0.00000  4.32261   4.32260   0.00
3    -1250.21762   -1250.21960   0.00000  3.54307  2.23320  4.32458   4.32260   0.00
4    -1250.21694   -1250.21695   0.00000  3.53501  0.00000  4.32526   4.32525   0.00
-----------------------------------------------------------------------------
Emin= -1250.21960
```

Figure 3. The typical output from the ANALYTIC script after analysis of DFT-NEB output.

4. Acknowledgement

5. References

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