Computational Materials Science 154 (2018) 449–458

Contents lists available at ScienceDirect

Computational Materials Science

journal homepage: www.elsevier.com/locate/commatsci

Understanding migration barriers for monovalent ion insertion in transition metal oxide and phosphate based cathode materials: A DFT study

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ARTICLE INFO

Keywords:
Li-ion
Na-ion
K-ion
Transition metal-ion cathode materials
Migration barriers
DFT calculations

ABSTRACT

High ionic conductivity is a prerequisite requirement for materials used in monovalent metal-ion rechargeable batteries. The extensive search of new electrode materials for Na-ion and K-ion monovalent metal-ion batteries requires a deep understanding of structural and chemical details of cation migration through the crystal lattice. In the paper, we consider three classes of transition metal oxide and phosphate cathode materials: AMn_2O_4 spinels, $AMPO_4$ olivines and $AVPO_4F$ tavorites ($A = $ Li, Na, K, $\square$; $M = $ Fe, Mn), used for pragmatic applications for secondary (rechargeable) batteries. Herein we examine Na^+ and K^+ migration characteristics in comparison with that of Li^+ by means of DFT + U, local energy calculations, empirical potentials, and bond valence energy landscape (BVEL). It is found that despite larger radii of Na^+ and K^+, the migration barriers are comparable with that of Li^+. In several cases, we reveal that the migration barrier of K^+ can be even lower than that of Li^+. This behavior is explained through the interplay of site and lattice energies during cation migration. For automation of screening of migration properties via DFT calculations, a new Python-based framework (SIMAN) is developed and benchmarked across three cathode materials structures.

1. Introduction

The portable electronic device revolution and upcoming transition to all electric vehicles (EV), heavily relies on Li-ion battery technology, which has led to a doubling of the prices for Li precursors in several years [1]. As a result, the interest in the alternative potentially cheaper battery systems, such as Na-ion (NIB) and K-ion (KIB) has been reignited [2,3]. Remarkably, owing to the negligible contribution of Li to the mass and cost of Li-ion cell (~3%), the price of Li itself has little effect on the battery prices [4]. For example, the use of Al anode current collector in NIB and KIB systems can provide greater cost reductions [2]. A more convincing reason to study alternative chemistries is the highly uneven distribution of Li across the continents [5]. Looking ahead, the worldwide transition to EV would exhaust the seemingly plentiful global terrestrial lithium reserves, even with the extensive recycling, not to mention the battery demand for larger scale needs such as grid storage [6]. Probably the most motivating reason to develop NIB and KIB relies upon the highly variable chemistries above known and better understood LIBs crystal structures, which provides great impetus to outperform Li-ion systems especially in grid-scale applications. However, this requires discovery of new cathode, anode, and electrolyte materials, as the existing NIB and KIB are usually more limited than LIBs, including the most decisive parameter, such as cost per Watt-hour [2].

One emerging and promising approach for materials discovery is to develop high throughput computational screening methods with respect to identifying specific properties [7]. One of such properties, essential for battery materials, is high ionic conductivity of charge carrier ions. However, the direct calculation of conductivity for example with density functional theory (DFT) is fairly complicated, hindering its usage in high-throughput screening. Therefore various models based on descriptors that correlate with barriers have been developed [8]. To improve the predictive power of such models it is important to understand the underlying physics of the diffusion process at the atomic level.

The influence of chemical composition and crystal structure on the diffusion process was systematically studied with DFT methods [9–11]. Leaving aside the statistical nature of the diffusion phenomena, the essential parameter that determines diffusion coefficient is activation energy (migration barrier) required for an atom to hop from one lattice site to another. The following features of the atomic structure were found to determine the migration barrier: (i) a number of vacancies involved in the atomic hops (layered oxides and sulfates) [12,13]; (ii) change of lattice constants due to cation extraction (layered materials) [14]; (iii) change of the transition metal (TM) oxidation state due

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https://doi.org/10.1016/j.commatsci.2018.07.057
Received 25 May 2018; Received in revised form 27 July 2018; Accepted 28 July 2018

to cation extraction [15]; (iv) Jahn–Teller distortion corresponding to the TM state through the change of the distance between the adjacent O ions ($LiTi_2O_4$ example) [16,17]. The mentioned effects are responsible for concentration dependence of the cation diffusion coefficient.

In addition to the mentioned factors, it is highly tempting to establish a quantitative relationship between migration barrier and local atomic structure for the given chemical composition. The simplest geometrical approach based on the open space metrics proved to be of limited use, mainly for a preliminary tentative analysis, while more reliable chemistry-related methods are still being developed [18]. It is hard to judge whether the same factors affect migration barriers for Li^+, Na^+ and K^+ cations. The comparison of Li^+ and Na^+ diffusion in layered and olivine structures was done by Ong et al. [19], by whom it was found that the migration barriers for Na^+ can be lower in layered structure but higher in olivine structure, than that for Li. Only few studies of cation migration were done for K. It is still not clear whether the migration barriers for K^+ should be larger than that for Li^+ and Na^+. One of the most appropriate tools to solve this problem is DFT that provides detailed information on the deformation of the local atomic structure during migration, as well as relaxation effects and charge redistribution.

In the current work, we study the migration of cations in cathode materials using DFT, extending it to Na and K containing materials. As a straightforward approach, we consider several most efficient Li-ion cathode materials belonging to oxide ($LiMn_2O_4$), phosphate ($LiMPO_4$), and fluoride-phosphate ($LiVPO_4F$) classes and their Na- and K-substituted structural analogues taking into account that an electrochemical exchange of Li^+ by Na^+/K^+ is widely adopted as an efficient approach in the experimental design of new cathodes [20,21]. Since this approach usually results in stabilizing metastable structures, it gives a unique opportunity to compare the influence of cation size in the equivalent crystal structures. In addition to that, we calculate migration barriers of Na and K in thermodynamically stable structures.

Considering several different crystal structures in two concentrations (initial and deintercalated states) and for three cations requires performing hundreds of DFT calculations. To maximize the efficiency and reduce time-costs we employed our custom-developed package SIMAN for automation of the DFT calculations, which is first-time introduced in this paper.

In Sections 2 and 3 we present calculation details and developed package SIMAN, respectively. In Section 4 we report crystal and electronic structures of considered compounds as well as intercalation voltages and volumes for Li, Na, and K. In Section 5 we present migration barriers calculated with DFT/DFT + U and discuss their correlation with different geometry and energy descriptors. The conclusions are provided in the final section.

2. Computational methodology

All DFT calculations are performed in VASP program [22] using generalized gradient approximation (GGA) to exchange-correlation functional and standard PAW PBE potentials [23] with minimum number of valence electrons. Tetrahedron method with Blöchl corrections is used for Brillouin-zone integrations [24]. The energy cut-off is fixed at 400 eV, the k-point density is between 0.2 and 0.3 $Å^{-1}$. The DFT + U calculations are carried out using Dudarev scheme [25]. The values of U are the same as in the work of Jain et al. [26]: 4, 3.9, and 3.1eV for Fe, Mn, and V, respectively. To improve the wave-function convergence the U-ramping approach is employed [27].

To eliminate Pulay errors the lattice optimization (ISIF = 4) is performed at constant volume for several contracted and expanded cells (7 points). The size of the supercell used in calculations of ion-diffusion barriers is about 10 Å, corresponding to one hundred atoms on average. The maximum force permitted for any vector component is 0.02 eV/Å except for $KVPO_4F$ and $KMnPO_4$ with K vacancies, where the maximum forces are 0.2 eV/Å and 0.17 eV/Å.

The migration barriers are determined using nudged elastic band (NEB) method as implemented in VASP. The method allows to find minimum energy path, which includes several intermediate configurations (images) between initial and final states. Since, the geometry of pathways in the considered materials is simple, only three intermediate images are used.

In addition to DFT-NEB, accessible pathways for mobile ions in the structure and migration barriers have been estimated with Bond valence energy landscape (BVEL) methodology. It is based on the empirically established relationships between the bond length, R, and the so-called bond valence, V defined by the formula [28]

$$V_{A-X} = \exp\left(\frac{R - R_0}{b}\right), \tag{1}$$

where R_0 and b are tabulated constants. Regions of a structure, where the BV sum, $V(A) = \sum V_{A-X}$, over all adjacent counter-ions X is close to the “ideal valence”, $V_{id}(A)$, or in other words the absolute value of its oxidation state (1 in case of Li, Na and K), are considered suitable for migration of Li^+, Na^+ and K^+. To convert the BV values into the site energy, $E(A)$, a Morse-type interaction potential is used. For BVEL calculations we use the 3DBVSMAPPER program, which generates a spatial distribution of $E(A)$ energy values within the entire unit cell [29]. The resulting three-dimensional grid can be adjusted by the activation energy parameter [E_{act}, i.e. the difference between the cut-off value of $E(A)$ and minimum $E(A)$, E_{min}] to locate and visualize the most energetically favorable areas for a particular ion. The minimum E_{act} value required for the areas to merge into a continuous system can be considered as an energy barrier within this approach.

The average intercalation voltages are calculated according to the following equation (on the example of $LiMn_2O_4$):

$$\overline{V} = \frac{E(\mathrm{Li}_{x1}\mathrm{Mn}_2\mathrm{O}_4) - E(\mathrm{Li}_{x2}\mathrm{Mn}_2\mathrm{O}_4) - (x1-x2)E(\mathrm{Li})}{x1-x2}, \tag{2}$$

where $E(\mathrm{Li}_x\mathrm{Mn}_2\mathrm{O}_4)$ is the full energy of the supercell with x Li atoms and $E(\mathrm{Li})$ is the energy of bcc-Li per atom. The average potential and volume changes are calculated for $x1 = 1$ and $x2 = 0$. All DFT calculations are performed using a specially developed SIMAN package, described in the next section.

3. Python package SIMAN

To process large number of similar DFT calculations we developed a management package SIMAN, written in Python programming language. The primary goal of SIMAN is to provide a platform for smart generation of input for DFT codes, such as VASP, batch submission of jobs, and extraction of output results in concise, ready for analysis form on the local computer. Thus, each calculation is represented as a special object, which is persistently stored in the database dictionary. For convenient addressing of the database a special naming convention is proposed. The key of each calculation should consist of three elements: the name of the atomic structure, the name of parameters set, the version of the structure. This naming system allows for keeping identical atomic structures calculated with various parameter sets and under different conditions, straightforward comparison of different structures for the same set of parameters, and an account of deformed structures by assigning them with a unique version number.

3.1. Reading atomic structures and input parameters

The initial atomic structure can be provided from common atomic data format files:

```
Li = smart_structure_read('Li2bcc.cif')
```

or obtained from Materials project database [30]: