

## Hybrid functional study on diffusion of silicate cathode material $\text{Li}_2\text{NiSiO}_4$

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**Abstract.** The orthosilicate systems  $\text{Li}_2\text{MSiO}_4$  ( $M = \text{Fe}, \text{Mn}, \text{Co}$  and  $\text{Ni}$ ) are recently believed to be a promising alternative to the olivine phosphates. In this paper, we present an interpretation of the diffusion mechanism for polaron-Li vacancy complexes in  $\text{Li}_2\text{NiSiO}_4$  based on the hybrid functional method HSE06. A comparison between the results obtained by GGA+U and HSE06 methods is carried out. The results confirm that the HSE06 method succeeds in describing the polaron localization in  $\text{Li}_2\text{NiSiO}_4$ . A polaron-Li vacancy complex model (V. A. Dinh *et al.*, *Appl. Phys. Express*, **5**, 045801 (2012)) is used to handle the explanation of the diffusion mechanism in this material. Four elementary diffusion processes for the polaron-Li vacancy complex are investigated and the preferable diffusion pathways are constructed by combining the possible elementary processes. It is found that the Li diffusion may proceed along the two preferable pathways in the [100] and [001] directions with the activation barriers of 1.17 and 0.96 eV, respectively. Furthermore, the accompanied migration of polaron can enhance the diffusion rate of Li ion in  $\text{Li}_2\text{NiSiO}_4$ .

### 1. Introduction

Li ion batteries are considered to be one of the most powerful, convenient and safe power sources [1]. However, the cathode material is still facing many disadvantages that should be overcome. One of the highly appreciated cathode materials is  $\text{LiFePO}_4$  due to its good thermal and chemical stability [2,3]. More recently, many researches have clarified that the orthosilicate system  $\text{Li}_2\text{MSiO}_4$  ( $M = \text{Fe}, \text{Mn}, \text{Co}$  and  $\text{Ni}$ ) can be an alternative to the olivine phosphate by reason of its strong Si-O bond which promotes a similar structure stability as in olivine phosphate [4].  $\text{Li}_2\text{MSiO}_4$  possesses many characteristics of an appealing cathode material such as high capacities, safe and low cost [5-9]. Especially the possibility of extraction of two lithium ions per formula unit makes this material the most promising cathode material. Hence, studying well the orthosilicate system is becoming an urgent issue. The ability of getting high capacity of  $\text{Li}_2\text{FeSiO}_4$  and  $\text{Li}_2\text{MnSiO}_4$  systems have been reported [10,11]. Having the same structure, Ni system is believed to have such advantages. However, to our knowledge, there is very few research on Ni system, hence, having a thorough study on Ni system is an urgent issue to have a complete picture on the hot material  $\text{Li}_2\text{MSiO}_4$ .

Ionic conductivity is one of the important features related to the performance of batteries and hence upgrading the ionic conductivity becomes a necessary mission. Having a thorough interpretation of the diffusion in the material is required for an understanding of conductivity. In olivine phosphate system, introducing a vacancy into the cell should lead to the formation of a bound polaron. Recently, a polaron-Li vacancy complex model has been proposed by Dinh *et al* [12] for the olivine system and



this model has been successfully applied for  $\text{Li}_2\text{FeSiO}_4$  [13]. In  $\text{Li}_2\text{NiSiO}_4$  system, the Li diffusion could also be regarded as a polaron-Li vacancy complex diffusion. In this paper, we give out an understanding of the nature of the diffusion mechanism by revealing elementary diffusion processes in  $\text{Li}_2\text{NiSiO}_4$ . Aiming to the task, we first figure out the formation of the bound polaron as a Li ion is extracted from the lattice. Then, we explore the diffusion of Li ion in the manner accompanying with the migration of its bound polaron. During each step, those two accompanied motions would form an elementary diffusion process. Finally, the preferable diffusion pathways will be revealed by combining the possible elementary diffusion processes.

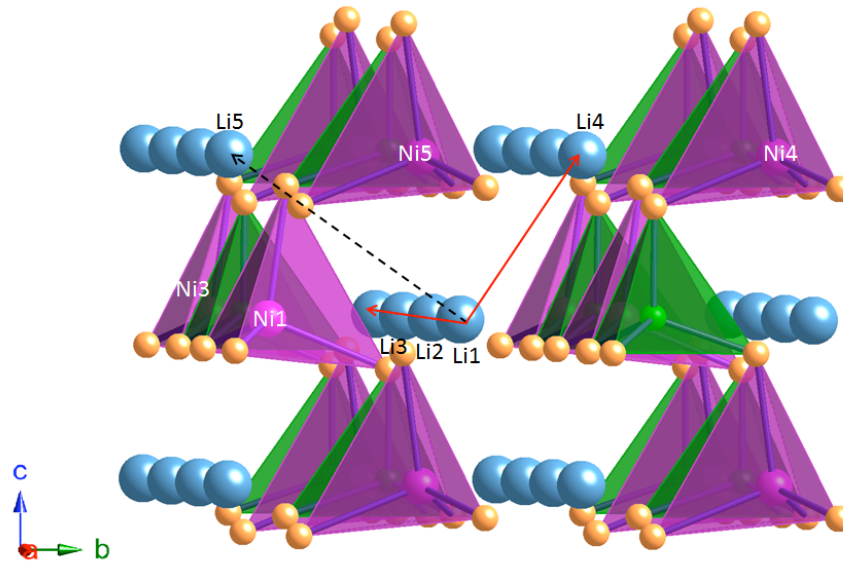


Figure 1. a) Crystal structure of  $\text{Li}_2\text{NiSiO}_4$  in the  $Pmn2_1$  symmetry, and schematic of diffusion paths viewed in the  $[100]$  direction. Ni tetrahedra and Si tetrahedra are illustrated in pink and green, respectively. Li atoms are shown in cyan. The red and black dash lines represent the moving paths of the Li ions in the elementary diffusion processes.

## 2. Methodology

During our calculation, the Vienna ab initio simulation package (VASP) [14-17] is used within density functional theory (DFT). Two methods are applied to deal with the calculation: Generalized gradient approximation (GGA) [18] and Hybrid density functional (HSE06) [19,20]. Within GGA method, the on-site coulomb term  $U$  has been taken into account to deal with electron-electron interaction on the Ni site. The on-site Coulomb term  $U$  and the exchange term  $J$  can be embedded into equation  $U_{\text{eff}} = U - J$ .  $U_{\text{eff}}$  is set at 6eV [9]. To our knowledge, GGA+ $U$  can solve effectively the diffusion problem in  $\text{Li}_2\text{FeSiO}_4$  as well as  $\text{LiFePO}_4$ , however, it fails in describing the polaron localization in  $\text{LiMnPO}_4$  [12,21]. Recently, the HSE06 method is proved to be a reliable tool that can predict such properties as crystal structure, bulk moduli, and band gaps effectively [19,20]. Especially, it can solve the problem of polaron localization in  $\text{LiMnPO}_4$  in a proper way [12]. Through our calculation, a  $2 \times 2 \times 2$  k-points grid [22] in GGA+ $U$  calculation and the center  $\Gamma$ -point in HSE06 calculation for a  $2 \times 2 \times 2$ -supercell were used, and the full relaxation was performed for all of the perfect and defect configurations. The cut-off energy was set at 500eV. The activation energy of each diffusion pathways was calculated by using the climbing image nudged elastic band (CINEB) [23] method within the HSE06 framework.

Similar to the other materials in the family of  $\text{Li}_2\text{MSiO}_4$ ,  $\text{Li}_2\text{NiSiO}_4$  is most frequently observed in the  $Pmn2_1$  space group with the orthorhombic structure [7,8]. The previous GGA+ $U$  calculation [9] showed that the lattice parameters of  $\text{Li}_2\text{NiSiO}_4$  are:  $a = 6.274$  (Å),  $b = 5.365$  (Å),  $c = 4.921$  (Å). The cell is arranged in corrugated layers where tetrahedral  $\text{SiO}_4$  and  $\text{NiO}_4$  lying alternatively on  $ab$ -plane linked by  $\text{LiO}_4$  tetrahedral along the  $c$ -axis as shown in figure 1. The  $\text{LiO}_4$ ,  $\text{SiO}_4$  or  $\text{NiO}_4$  tetrahedral compose of one Li, Si or Ni atom locates in the central site surrounded by the oxygen tetrahedral. As mention above, there is only corner sharing between tetrahedral, each  $\text{SiO}_4$  or  $\text{NiO}_4$  tetrahedral shares

its four corners with each other.  $\text{LiO}_4$  tetrahedral lies between the two  $[\text{SiO}_4$  and  $\text{NiO}_4]$  layers. In this space group, there are two formula units per unit cell which includes four Li, two Ni, two Si and eight O atoms.

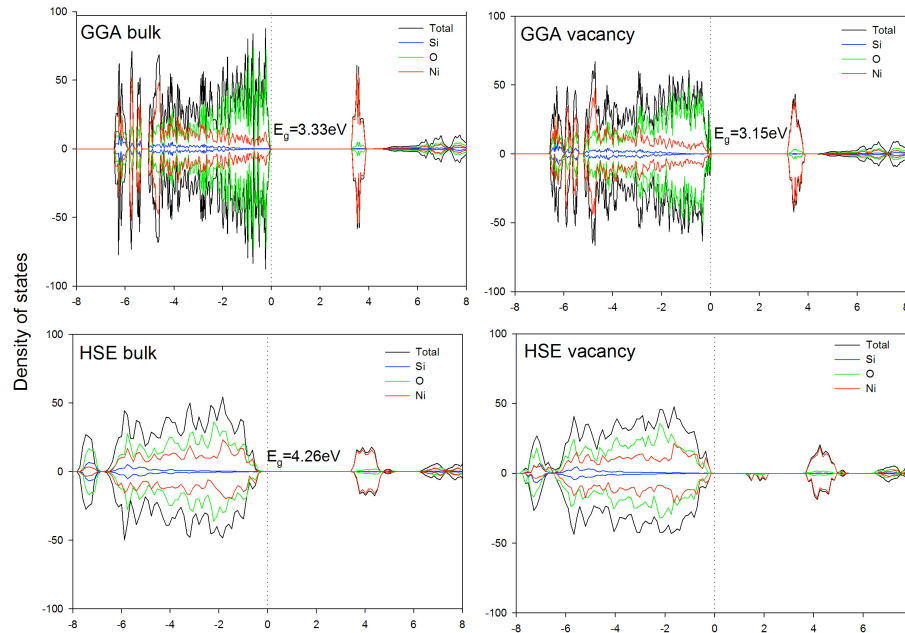


Figure 2. DOS of  $\text{Li}_{32}\text{Ni}_{16}\text{Si}_{16}\text{O}_{64}$  and  $\text{Li}_{31}\text{Ni}_{16}\text{Si}_{16}\text{O}_{64}$  obtained by GGA+U and HSE methods. Positive (negative) value of DOS indicates the majority (minority) spin.

### 3. Results and discussion

#### 3.1 Structural, electronic properties and polaron formation

Table 1 illustrates the structure parameters obtained by GGA+U and HSE06 methods for the perfect structure of  $\text{Li}_2\text{NiSiO}_4$ . The result of HSE06 is compared with GGA+U in a percentage. For the perfect structure, the GGA+U and HSE06 methods give the similar structure parameter in x-direction. The lattice parameters obtained by HSE06 are:  $a = 6.290$  (Å),  $b = 5.299$  (Å),  $c = 4.856$  (Å) and the volume is slightly smaller than that by GGA+U (2.67%) as indicated in table 1.

We present here the GGA+U and HSE06 study of density of states (DOS) in figure 2 for further understanding of the electronic structure of the material. The total DOS, partial DOS (PDOS) of Ni, O, and Si atoms are illustrated. The two approaches yield quite similar band gap in perfect structure. The material exhibits the characteristic of an insulator with a band gap of 3.33eV obtained by GGA+U, or 4.26eV obtained by HSE06. Apparently in vacancy structure, the two calculation method produces different DOS pictures. When a Li vacancy is introduced to the lattice, the  $\text{Ni}^{2+}$  ion which is a neighbor to the vacancy will be oxidized to  $\text{Ni}^{3+}$  resulting in the 3d localized states of  $\text{Ni}^{3+}$  appearing in the band gap. The appearance of these bound states in the band gap is confirmed by the electronic structure picture of HSE06 whereas those bound states could not be found in GGA+U result. This expresses the possibility of localizing the polaron formation of HSE method. Therefore, from now on, only the result within HSE06 method is represented.

Table 1. Calculated lattice parameters and band gap energy.

$\text{Li}_2\text{NiSiO}_4$	$a/\text{\AA}$	$b/\text{\AA}$	$c/\text{\AA}$	$V/\text{\AA}^3$	Band gap/eV
HSE	6.290	5.299	4.856	161.85	4.26
GGA+U (U=6)	6.291 (0.02%)	5.368 (1.30%)	4.921 (1.34%)	166.17 (2.67%)	3.33

Generally, the removal of a Li atom would lead to the change of the oxidation of one of its neighboring Ni atom from 2+ to 3+; hence, the average Ni-O bond becomes shorter. Particularly, the shrinking of the average Ni-O bonds from 1.98 Å in Ni<sup>2+</sup>-O bond to 1.87 Å in Ni<sup>3+</sup>-O would lead to a local lattice distortion in which the charge carrier can be trapped. Consequently, a small polaron appears at a Ni<sup>3+</sup> site. Around each Li site, there are four nearest Ni neighbors and our energy calculation predicted that the polaron most favorably forms at the third nearest Ni neighbor.

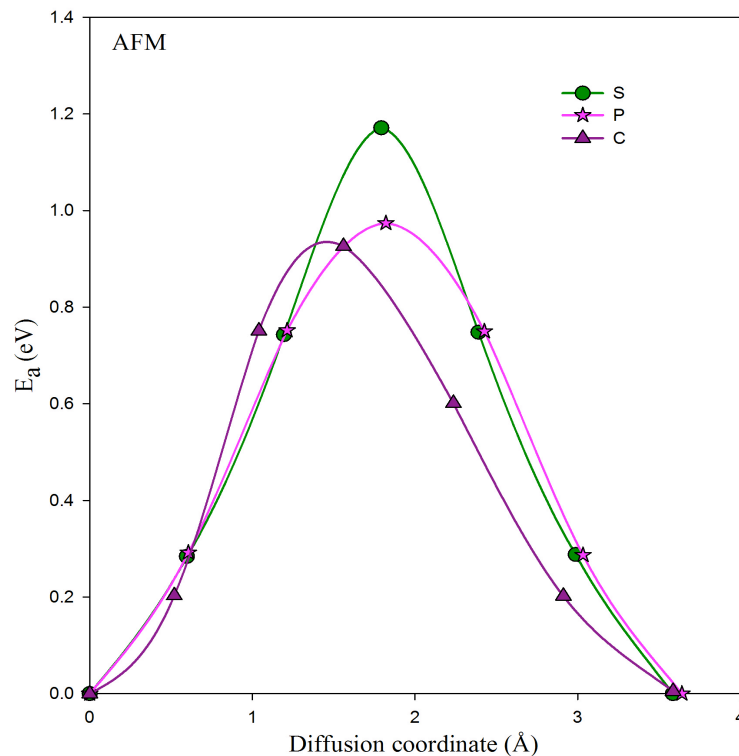


Figure 3. Calculated activation energy of polaron-Li vacancy complex diffusion in Li<sub>2</sub>NiSiO<sub>4</sub>. The green, pink and violet curves depict the activation energy profile of the preferable *single Li diffusion*, *parallel* and *crossing* processes, respectively.

### 3.2 Diffusion

As a vacancy is introduced to the lattice, some of neighboring Li atom would tend to hop to the vacancy site and cause the Li migration which takes places along an opposite path to the vacancy. During diffusion, the movement of the Li vacancy would be accompanied by the small polaron migration and would cause the polaron – Li vacancy complex diffusion [12]. Aiming at figuring out the diffusion properties of the material, we first investigate the elementary diffusion processes of the complex and then combine those processes to form the most preferable diffusion pathways. To make it easier to visualize, we mark the Li diffusion path as red and dashed black arrows as shown in figure 1. Four elementary processes are investigated: two intra-layer processes along the [100] direction (S and P) and two inter-layer processes in the (100) plane (C and T). As shown in figure 1, The Li atom are denoted as Li<sub>*i*</sub> (*i* = 1→5) and its accompanied polaron sites are indexed as Ni<sub>*j*</sub> (*j* = 1, 3→5), correspondingly. Figure 4 illustrates possible diffusion pathways by combining elementary processes while figure 3 presents activation barriers of elementary processes. The diffusion mechanism of four elementary processes and possible pathways are described as follow:

i) Process S and P: letters S and P are denoted “*Single*” and “*Parallel*”. In process S, the Li vacancy diffuses from the site Li<sub>1</sub> to Li<sub>2</sub>, and then in process P, the vacancy moves from Li<sub>2</sub> to Li<sub>3</sub>. Since the vacancy at Li<sub>1</sub> and Li<sub>2</sub> possess the same accompanied polaron; Ni<sub>1</sub>, then the polaron may stand still during the Li diffusion in process S. There is only the Li vacancy diffusion in this process and that is the reason why it was called *Single Li diffusion* (S) [13]. The activation barrier of this

process is 1.17 eV (figure 3). Within P process, the polaron migration is included. When the Li vacancy jumps from  $\text{Li}_2$  to  $\text{Li}_3$ , the polaron at  $\text{Ni}_1$  should consequently hop to  $\text{Ni}_3$  along parallel route to the one taken by the Li vacancy. Then, this process is named as *Parallel diffusion* (P) [13]. According to the activation barrier profile in figure 3, it costs 0.98 eV for the polaron - Li vacancy complex to diffuse in this process. The complex parallel diffusion has a lower barrier than the single Li ion diffusion. Thus, in contrast to the  $\text{Li}_2\text{FeSiO}_4$  [13], the accompanied polaron migration in  $\text{Li}_2\text{NiSiO}_4$  can enhance the diffusion of Li ions. In these processes, the Li vacancy diffuses through a parabolic path with an equal distance of 3.60 Å as illustrated by the green and pink dash curves in figure 4(a). By joining these processes, we can obtain a possible diffusion pathway along which Li ions diffuse through a straight line in the [100] direction.

ii) Process C: the letter C stands for “*Crossing*”. When the vacancy at the  $\text{Li}_1$  site jumps diagonally upward to occupy the  $\text{Li}_4$  site, the accompanied polaron at  $\text{Ni}_1$  would consequently jump to  $\text{Ni}_4$ . The polaron migrates across the Li diffusion route through neighboring Fe layers, hence, the name *Crossing diffusion* is given for this path [13]. The Li vacancy has to travel a distance of 3.60 Å. The activation barrier of the polaron – Li vacancy complex diffusion through this process is 0.93 eV. A zigzag pathway as illustrated in figure 4(b) can be formed by replicating this process within the (100) plane along the [001] direction.

iii) Process T: the letter T stands for “*Through*”. Along with the diffusion of the Li vacancy from  $\text{Li}_1$  to  $\text{Li}_5$ , the polaron will simultaneously jump from  $\text{Ni}_1$  to  $\text{Ni}_4$ . *Through layered* (T) was named to this process because the Li vacancy diffuses through Ni-Si layers, as seen in figure 1. The diffusion distance for this process is 4.64 Å which is quite far for Li to travel. Because the complex has to travel a long distance through the screening Ni-Si layers, it costs as high as 2.12 eV to diffuse. It would be hardly for the complex to diffuse with such high activation energy. Hence, this process should not contribute to the possible pathway and we can ignore it.

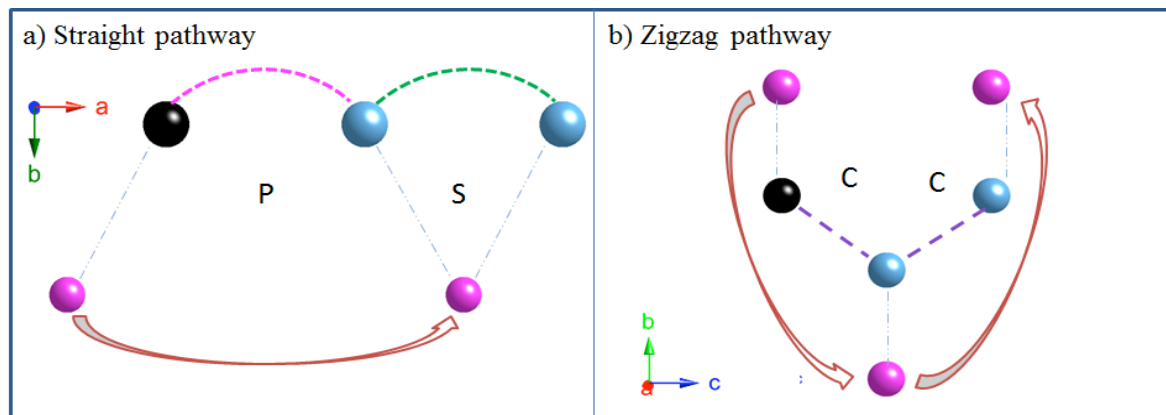


Figure 4. Schematic of possible diffusion pathways. Li vacancy and its accompanying polaron are “connected” by blue dash-dotted-dash lines. The green, pink and violet dash curves correspond to the single Li diffusion, parallel and crossing processes, respectively. The polaron migration is indicated by red arrows.

In summary, we have carefully studied the formation of polaron and the diffusion mechanism of the complex polaron-Li vacancy in  $\text{Li}_2\text{NiSiO}_4$ . One more time, the HSE06 method is proved to succeed in describing the polaron localization in the cathode materials. An investigation of the four elementary diffusion processes was carried out for an insight view of diffusion mechanism, and three processes were found to be preferable. Combining three favorable processes, we figured out the two most preferable diffusion pathways: straight and zigzag pathways. The complex diffusion through the [100] and [001] directions have the activation barriers of 1.17 eV and 0.94 eV, respectively. Similar to  $\text{Li}_2\text{FeSiO}_4$ , the diffusion in the Ni system is also two dimensional. However, in contrast to  $\text{Li}_2\text{FeSiO}_4$ , the Li ion diffusion in  $\text{Li}_2\text{FeSiO}_4$  can be enhanced by its accompanied polaron migration. Finally, by means of HSE06, we have successfully investigated the structural and electronic structures, polaron formation, and the diffusion of the polaron-Li vacancy complex in  $\text{Li}_2\text{NiSiO}_4$ . With the possibility of

the two-redox-potential and the two-dimensional diffusion of Li ions,  $\text{Li}_2\text{NiSiO}_4$  can be considered as a promising cathode material for the rechargeable Li ion batteries.

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