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# First-principle study of Li ion diffusion in copper thin film*

Xiong Zhi-Hua(熊志华)[a)b)] and Lei Min-Sheng(雷敏生)[a)†]

[a)] *Department of Physics, Jiangxi Normal University, Nanchang* 330027, *China*

[b)] *Department of Applied Physics, Jiangxi Science & Technology Normal University, Nanchang* 330013, *China*

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The diffusion mechanism of Li ion in a copper thin film is investigated from first-principle calculations. The energy barriers for possible spatial hopping pathways are calculated with the adiabatic trajectory method. Theoretically, we have identified that Li-ions can diffuse through a copper thin film by successive nearest neighbour vacancy–atom exchanges at room temperature. It is found by comparing the different mechanisms that the nearest neighbour vacancy assisted jumping is highly probable. It is also confirmed that more free diffusion may be observed by increasing the number of copper vacancies in the thin film.

**Keywords:** diffusion barrier, lithium, copper thin film, Li-ion battery
**PACC:** 6780M, 8640, 3120A

## 1. Introduction

For Li-ion batteries, copper foil is the material commonly used for current collector of anode because it is stable in charge/discharge processes. Copper is known not to form any alloy with Li, implying that a free mass transfer of Li in copper film is improbable at an ambient temperature. Surprisingly, Suzuki *et al*[1] have discovered recently that the mass transfer of lithium ion in the copper lattice is possible even at room temperature. They have proved experimentally that Li moves freely through the copper film deposited on carbon. However, theoretical investigations on the diffusion have not been reported as yet. In order to understand the interesting phenomenon, several important issues need to be addressed. For instance, what is the most possible mechanism and pathway for Li ions to enter the Cu film interior? which defect promotes or hinders the diffusion? why more free diffusion can be obtained by increasing the number of copper vacancies?

To investigate these issues, first-principle calculations have been carried out where the motion of lithium ion in a copper film at room temperature is studied. In the present study, we focus on the energy barrier calculations in order to obtain possible mechanism and pathway for lithium ion diffusion in the copper thin film.

## 2. Details for calculation

For our calculations reported here, the Vienna *ab initio* simulation package (VASP)[2,3] that is described in detail elsewhere was utilized to perform the total-energy calculation and molecular-dynamics simulation. This method is a planar wave density functional theory (DFT) based on the projector-augmented-wave (PAW) potentials. All calculations have been performed using the generalized gradient approximation (GGA) of Perdew–Wang 91 (pw91).[4] Other computational details include the basis-set cutoff energies of 350eV and a Gaussian smearing scheme with a width of 0.2eV.[5] Brillouin zone (BZ) integration was performed using the special point sampling technique of Monkhorst and Pack[6] for these calculations. All atoms were allowed to relax until the force on each atom was below 0.1eV/nm. An equilibrium Cu lattice distance 0.364nm from bulk calculations, which is in good agreement with other calculated and experimental results,[7,8] was used throughout the present

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†E-mail: mslei@jxnu.edu.cn

study.

To model the copper thin film reported here, we used a super-cell model with six (111) slab layers separated by six vacuum layers to prevent interactions between adjacent slabs. As is well known, Cu (111) surface is not reconstructed. Therefore, the Cu (111) surface was used as an appropriate surface (i.e. the actual surface) to investigate the lithium diffusion in copper film in this work. A vacancy can be initially introduced by removing discretely one Cu atom from each atomic layer. The surface unit cell is of 3×3 structure and the total numbers of atoms in the super-cell are 54 and 53 for the perfect slab and for the vacancy system, respectively. According to the definition of the energy of vacancies formation, we have

$$E_v = E(N-1,V) - \frac{N-1}{N}E(N,0),$$

where $E(N-1,V)$ and $E(N,0)$ are the energies of slab with and without vacancy, respectively. This formula is widely used for calculating vacancy formation energy.[9,10]

To investigate the diffusion in the copper thin film, the system was modelled by a super-cell containing one Cu vacancy for the vacancy diffusion while the system was modelled by a super-cell containing one substitutional lithium ion and one Cu vacancy for the lithium ion diffusion. Then the "adiabatic trajectory method"[11−13] was used to determine the diffusion barriers of lithium in the copper thin film. In this method, the total energy was monitored while the Li was pushed through the copper thin film at a small and constant speed (e.g. the thermal speed at 300K) in a given direction. The diffusion energy barrier can be obtained from the difference between their total energies. Note that Li ion was constrained in one direction only. It could freely move in the direction perpendicular to the applied force, thereby could find its optimum path. All other atoms were relaxed continuously in response to the Li motion, subject to appropriate constraints in the case of transition states. This method is found to be a viable and realistic alternative to the time-consuming point-by-point determination of the potential energy surface.[11−13] Various diffusion paths and possible mechanisms will be discussed in detail in the next section.

# 3. Results and discussion

## 3.1. Vacancy formation energy

Two kinds of relaxation are involved in a vacancy calculation: the volumetric relaxation and the structural relaxation. It is found that the volumetric relaxation is irrelevant to the large unit cell in this work, but the structural relaxation is not the case. The structural relaxation is a local and slight effect. After relaxation the neighbouring atoms are drawn towards the vacancy to some extent when an atom is removed. According to the formula, the vacancy formation energy was calculated following the calculation of the total energy. As a comparison, the formation energy of the vacancy in bulk was also calculated using the same number of atoms. The calculated values listed in Table 1 show that the results obtained from different theories agree well with each other. It is clear that the vacancy formation energy of the (111) surface is lower and therefore contributes more to the mass transport, than that in the bulk. However, experimental data on point defects are deficient even for the already extensively studied copper thin film. Indeed it is not so easy to determine accurately the atomic quantities such as the formation energy of a single vacancy and that of an interstitial experimentally. Furthermore, these quantities are affected by the local environment of the defect, which is very difficult to probe.

**Table 1.** Formation energies (in eV) of the vacancy in the surface layer, subsurface layer and central layer, and their comparison between measurements and calculations using LDA.

| | Surface Layer | Subsurface layer | Central Layer | Bulk |
|---|---|---|---|---|
| GGA | 0.69 | 0.82 | 1.00 | 1.04 |
| LDA[14] | | 0.92 | | 1.29 |
| Exp.[15] | | | | 1.04 |

## 3.2. Vacancy diffusion

Various vacancy diffusion processes were studied in the present work. The vacancy in the copper thin film possibly moves to the 12 nearest neighbour sites and to the next nearest neighbour sites, etc. Figure 1 shows the energy change of Cu vacancy located in the subsurface moving to the surface. It indicates that the vacancy jumps to its nearest neighbour (NN) site and next nearest neighbour (NNN) site with a mini-

mum diffusion barrier of 0.71eV and 9.36eV, respectively. The NN jump-diffusion mechanism can be expected to be favorable in energy based on the fact that no disorder is created during jumping. In the copper thin film the substitution of a vacancy for one of its neighbours will lead to migration of a vacancy. That is to say, vacancies can move forward through simple vacancy-atom exchanges by the NN jump mechanism. Although this appears to be the most common vacancy-related diffusion mechanism, vacancies can also migrate by collective transitions involving two or more atoms. So, vacancies might represent in principle one of the channels that promote lithium ion diffusion by means of an NN hopping process. The Li/Cu(111) diffusion mechanism will be discussed in the next section.

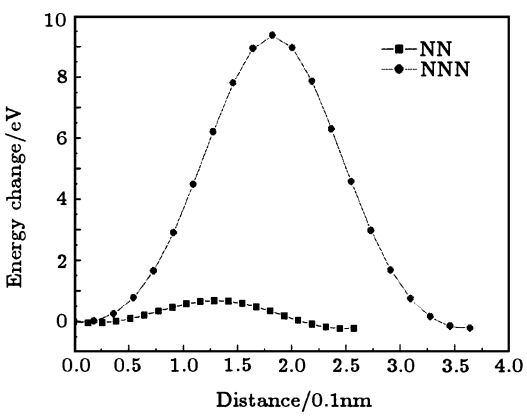



**Fig.1.** Energy barriers of vacancy diffusion to NN and NNN sites, the distances of NN and NNN are 0.2574nm and 0.3640nm, respectively.

### 3.3. Lithium diffusion barrier and mechanism

Our work shows that the incorporation of lithium ion with Cu vacancy resulting in the formation of a substitutional defect is more favorable than lithium ion alone on an interstitial site in the surface because the former shows a lower total energy. Therefore the above Li-substitution configuration is taken as the starting point. It has been mentioned that we focus on the energy barrier calculations in order to obtain possible mechanism and pathway for Li diffusion in the copper thin film. Using the "adiabatic trajectory method"[11−13] the different pathways are calculated for energy barriers of the possible diffusion of Li ions in the following. Table 2 shows various mechanism calculations of Li migration from surface layer to subsurface layer, Table 3 shows the energy barriers of Li diffusion inside each layer of copper film by NN vacancy assisted mechanism, and Table 4 shows the energy barriers of Li diffusion through six-layer copper thin film by NN vacancy assisted mechanism.

#### 3.3.1. Diffusion of lithium ion jumping into interstitial site

In this case, lithium ion alone in the lattice can form an interstitial defect. The diffusion path is considered between lithium ion and interstitial site. It seems to be the easiest way of diffusion conceptually because it involves the movement of a single species, a lithium ion. However, it is found that direct interstitial jumping is not favorable for lithium diffusion due to its high barrier. The atoms around the interstitial Cu are disordered during diffusion and the system becomes unstable because its energy is high. The calculated results show that in the case of Li diffusion from surface to the interstitial site located in subsurface, Li jumping into the center of three NN Cu atoms in the subsurface has a high diffusion barrier of 11.75eV.

#### 3.3.2. Diffusion of Li–Cu cooperating jump

We now consider another way of lithium diffusion in Cu film: Li–Cu cooperating jump. This is more complicated because several atoms move in a cooperative way. Two cases are discussed by taking into account the possible diffusion paths: lithium atom kicks a lattice atom out of its regular position (a) to another interstitial site or (b) to a vacancy, and then resides in place. These jumps occur almost at about the same time. In the first case, similar to the lithium jumping to the interstitial site alone, the diffusion barrier of this process is high. In the second case, there are also two possibilities: the jumping lithium ion, the NN cooperating Cu ion and the vacancy are in a line or not. This Li-Cu cooperating jump mechanism is shown in Fig.2. The energy barriers corresponding to these two cases are 1.98eV and 2.35eV, respectively. Clearly the cooperating jump in Li/Cu(111) is not quite possible because of the high jump barrier.

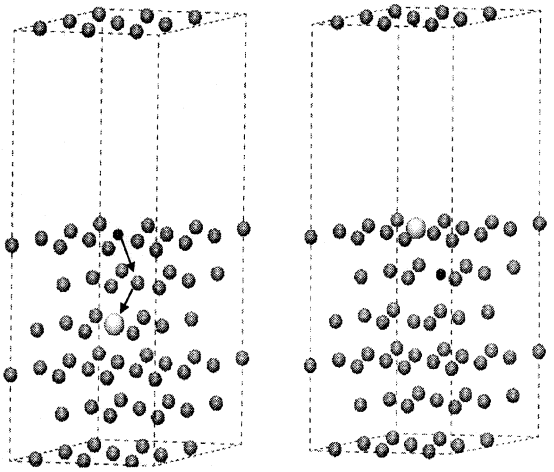


**Fig.2.** Diffusion of Li by the Li–Cu cooperating jump mechanism. Small black sphere denotes Li atom, and big white sphere and grey sphere represent the vacancy and the Cu atom respectively.

### 3.3.3. Diffusion of lithium and Cu by direct exchange

We consider the case where the substitutional lithium hops out of its site, and then an NN Cu atom jumps there to fill this vacancy, resulting in another vacancy. In the subsequent steps the lithium ion jumps into the vacant Cu position. If this process occurs Li–Cu will exchange their sites directly. However it is found that this direct mechanism does not contribute to the lithium ion diffusion in the copper thin film because of the high jump barrier of 20.21eV. To our knowledge, this process was experimentally verified[16] or theoretically explained[17] only in the case of diluted substitution boron atoms in copper metals. As the radius of Li ion is larger than that of B ion, it is more difficult for a lithium ion to diffuse in this way.

### 3.3.4. Diffusion of lithium by vacancy mediated

First, we consider that Li ion diffuses from surface layer to the subsurface layer. We choose a possible path from the Li site to the NN Cu vacancy, and another possible path is selected from the Li site to the NNN Cu vacancy for comparison. Calculations show that the barriers of the NN jumping and NNN jumping are 0.67eV and 4.47eV respectively. Both barriers, as illustrated in Fig.3, are located at a central point between lithium and vacancy. The barrier of NN jumping is significantly lower than that of the NNN jumping. In contrast, of all the possible diffusion mechanisms as listed in Table 2, the diffusion barrier by NN vacancy mediated is lowest. Clearly, NN vacancy assisted jumping is the most possible mechanism of lithium diffusion in copper film. That is, lithium diffuses in copper film mainly by successive vacancy–atom exchanges.

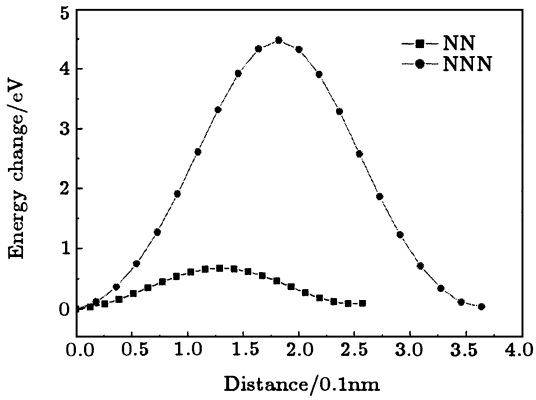



**Fig.3.** Energy barriers of lithium diffusion from surface layer to subsurface layer by NN and NNN vacancy assisted, the distances of NN and NNN are 0.2574nm and 0.3640nm, respectively.

**Table 2.** Energy barriers of Li migration from surface layer to subsurface layer, calculated with various possible mechanisms.

| Diffusion mechanism | Energy barrier/eV |
|---|---|
| Interstitial | 11.75 |
| Cooperating jump | 1.98 |
| Direct exchange | 20.21 |
| Vacancy assisted | 0.67 |
| Divacancies assisted | 0.41 |

Table 3 shows the energy barriers of Li diffusion inside each layer by NN vacancy assisted. It is found that these values are slightly smaller than those of the Li diffusion through copper thin film. For instance, the difference between the energy barrier of Li diffusion from surface to subsurface and that of Li diffusion from surface into surface layer is only as small as 0.09eV. It is also found, for the case of diffusion from surface to subsurface, the difference of energy barriers between Li diffusion assisted by vacancy and Cu vacancy diffusion is 0.13eV. That is to say, Li moves more easily than Cu vacancy does.

**Table 3.** Energy barriers of lithium diffusion inside each layer of copper thin film by NN vacancy assisted mechanism. Layers 1 and 6, layers 2 and 5, layers 3 and 4 are surface, subsurface, and central layers, respectively.

| Li migration inside each layer | Energy barrier/eV |
|---|---|
| Layer 1 | 0.58 |
| Layer 2 | 0.57 |
| Layer 3 | 0.64 |
| Layer 4 | 0.64 |
| Layer 5 | 0.58 |
| Layer 6 | 0.58 |

Table 4 shows the energy barriers of Li diffusion through the copper thin film with 6 atom-layers. The table includes five barriers that are slightly different. It is suggested that Li motion occurs predominantly by successive vacancy-atom exchanges and the mass transfer of Li ions in the copper film is possible if the vacant space is not occupied by copper ions.

**Table 4.** Energy barriers of lithium diffusion in six-layer copper thin film by NN vacancy assisted mechanism. Layers 1 and 6, layers 2 and 5, layers 3 and 4 are surface, subsurface, and central layers, respectively.

| Li migration through two neighbour layers | Energy barrier/eV |
|---|---|
| Layer 1 → 2 | 0.67 |
| Layer 2 → 3 | 0.63 |
| Layer 3 → 4 | 0.64 |
| Layer 4 → 5 | 0.62 |
| Layer 5 → 6 | 0.67 |

Based on the above calculated results, we deduce that Li diffuses freely inside each layer by vacancy-atom exchange because of the energy barriers being low, meanwhile the Cu vacancy also moves due to the migration barriers not being high. When Li becomes the NN of the vacancy located in next layer, Li migration through neighbour layers will possibly occur by NN vacancy mediated mechanism.

### 3.4. Diffusion of lithium in some actual cases by vacancy mediated mechanism

Actually vacancies may result from, for example, impurities and radiation damages in a material. Then what is the diffusion barrier? Suzuki *et al*[1] believed that the lithium ion could move freely in the lattice during the lattice vibration and periodically enlarge the vacant space if the vacant space in metallic copper was larger than the diameter of unsolvated lithium ion. Consider a stable configuration of two Cu vacancies. It is found when the two vacancies are on NN sites, the total energy of the system is 0.27eV lower than when they are isolated. In other words, the formation of divacancies can make the system more stable. The diffusion barrier of lithium jumping to the NN divacancies is estimated at 0.41eV, lower than that of the diffusion between lithium and Cu monovacancy around it. Figure 4 shows the energy barriers with monovacancy and divacancies. Our results suggest that the additional Cu vacancies introduced into the material can accelerate the diffusion rate of lithium. However, if these extra vacancies are created by introduction of impurities, it is possible that these impurities will hinder lithium ion diffusion, a negative effect. This suggestion needs to be confirmed in the future work.

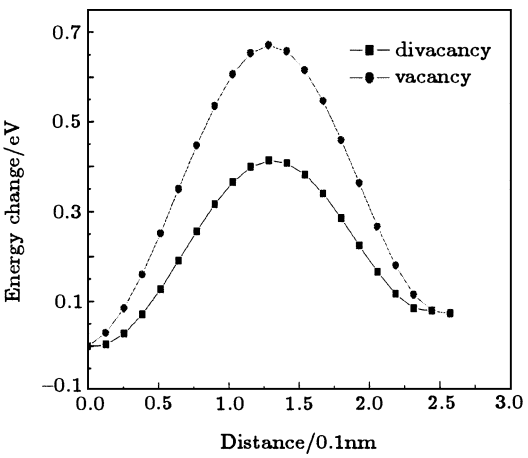



**Fig.4.** Energy barriers of lithium diffusion from surface layer to subsurface layer respectively by vacancy and divacancy assisted.

We also calculated the energy barrier of Li diffusion in a thicker copper thin film (for instance with ten layer) from surface layer to subsurface layer by NN vacancy assisted mechanism. It is found that the barrier is of 0.64eV, which is slightly lower than that of the six-layer copper thin film. This suggests there exists a relationship between the diffusion barrier and the thickness of the copper film. We think this may give a theoretical guidance for optimizing the performance of lithium ion battery, and we could design the reasonable thickness of Cu film to obtain the optimal performance. Certainly, this suggestion also needs to be identified in the future work.

From what has been discussed above, we may also draw the conclusion that Li can diffuse in copper thin film by vacancy-mediated mechanism.

## 4. Summary

In conclusion, first-principle density-functional calculations are performed for lithium ion migration in a copper thin film. The energy barriers corresponding to various diffusion processes are calculated in the paper. Theoretically, we have proved that Li can diffuse through the copper thin film by NN vacancy assisted mechanism. We have also explained why more free diffusion may be observed by increasing the number of copper vacancies in the thin film though other factors may also affect the benefits gained in this case. In

any case, NN hopping is an optimal diffusion mechanism. Therefore, lithium ion can transport in the copper lattice via vacancy-mediated process at room temperature.

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## References

[1] Suzuki J *et al* 2001 *Electrochem. Solid-State Lett.* **4** A1
[2] Kresse G and Hafner J 1993 *Phys. Rev.* B **47** 558
[3] Kresse G and Furthmüller J 1996 *Phys. Rev.* B **54** 11169
[4] Perdew J P *et al* 1992 *Phys. Rev.* B **46** 6671
[5] Methfessel M and Paxton A T1989 *Phys. Rev.* B **40** 3616
[6] Monkhorst H J and Pack J D 1976 *Phys. Rev.* B **13** 5188
[7] Wang G C and Yuan J M 2003 *Acta Phys. Sin.* **52** 4 (in Chinese)
[8] Crljen Ž *et al* 2003 *Phys. Rev.* B **68** 195411
[9] Vita A D and Gillan M J 1991 *J. Phys. Condens. Matter* **3** 6225
[10] Mehl M J and Klein B M 1991 *Physica* B **172** 211
[11] Zhang Q M *et al* 1995 *Phys. Rev. Lett.* **75** 101
[12] Wang C *et al* 1992 *Phys. Rev. Lett.***69** 3789
[13] Meunier V *et al* 2002 *Phys. Rev. Lett.* **88** 075506
[14] Polatoglou H M, Methfessel H and Scheffler M 1993 *Phys. Rev.* B **48** 1887
[15] Boer F R de *et al* 1988 *Cohesion in Metals* (North Holland: Amsterdam) p108
[16] Ittermann B *et al* 1996 *Phys. Rev. Lett.* **77** 4784
[17] Stöckmann H J *et al* 2001 *Phys. Rev.* B **64** 224301