**Theoretical insight into charging process in a Li_3PO_4 (100)/ LiFePO_4 (010)
coherent interface system**

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Abstract

We have investigated the introduction of Li vacancy ($V_{Li}^{\bullet}$ in the Kröger-Vink notation) into a Li_3PO_4 (100)/ $LiFePO_4$ (010) coherent interface with the density functional theory in order to gain an insight into the initial stage of the charging process. The $V_{Li}^{\bullet}$ introduction results in the formation of a Li ion vacancy ($V_{Li}^{\bullet}$) and hole (h). When one $V_{Li}^{\bullet}$ is introduced in each bulk $LiFePO_4$ and Li_3PO_4 materials (both $V_{Li}^{\bullet}$ and h are donated to the position in the proximity of the initial $V_{Li}^{\bullet}$ position), the formation energies of the Li vacancy (E_V) are quite different between them. On the other hand, when introduce into the $Li_3PO_4/LiFePO_4$ interface system, the values of E_V in the $LiFePO_4$ and Li_3PO_4 bulk regions of the interface become almost equal. This is because irrespective of the introduced $V_{Li}^{\bullet}$ position, the associated h is always donated to the $LiFePO_4$ region while the Li_3PO_4 region keeps its insulating properties. Although the Li atoms near the interface have smaller E_V than in the bulk regions, it is suggested that only a fraction of them may be extracted at the initial stage of charging which is not enough to lead to the Li depletion at the interface and as a result the effect of the space charge layer may be negligible in the $Li_3PO_4/LiFePO_4$ interface.

Keywords: Li vacancy formation energy; Density functional theory; Interfacial resistance

1. Introduction

All solid-state lithium ion secondary batteries are expected as the next generation of batteries [1,2]. Because traditionally used flammable electrolytes are replaced by solid electrolytes, much improvement is expected in safety and cyclic performance. In spite of the great benefits, however, the practical use of solid electrolytes has still some issues. Large interfacial resistance is one of them, which hampers fast charging and discharging processes. The interfacial resistance is divided into two types. One is due to the grain boundaries in the bulk electrode and electrolyte materials and the other is due to the interfaces between the electrolyte and electrode. Heat treatment is a possible method to decrease the interfacial resistance in the grain boundary, while it increases the interfacial resistance at the solid electrolyte and electrode interface [2]. The expected benefit of using solid electrolytes is ruined in the process of fabrication. To explain the interfacial resistance several mechanisms have been proposed so far such as the formation of a space charge layer [2], the formation of harmful interface products [3] and so on. For the next generation batteries, there are several candidates as electrode materials and both solid oxides and sulfides are used as electrolytes. The origin of the interfacial resistance may depend on the pairs of the electrolyte and electrode materials. The reasonable explanation of the interfacial resistance are strongly demanded based on the detailed structures of the electrolyte and electrode interfaces.

The oxide Li_3PO_4 is often used as solid electrolytes. Recently, the interface between N-doped Li_3PO_4 and LiCoO_2 is reported to exhibit a low resistance in thin-film batteries [4]. The coating by Li_3PO_4 is also known to be an effective method to improve the poor conductivity of LiFePO_4 [5]. These experiments suggest that the interfaces between the solid oxide electrolyte Li_3PO_4 and the oxide electrodes LiFePO_4 and LiCoO_2 may exhibit low interfacial resistances. However, the details of the interface properties have yet to be elucidated.

In this study, we consider the $\text{Li}_3\text{PO}_4/\text{LiFePO}_4$ interface. LiFePO_4 is expected as an environmentally-friendly and cheap cathode material for the next generation batteries. Similarities

in the elemental composition and cell parameters between γ -Li₃PO₄ [6] and LiFePO₄ [7] enable us to make the Li₃PO₄ (100)/LiFePO₄ (010) coherent interface theoretically, as reported in our previous study [8]. Here, we have investigated the electronic structures of the Li₃PO₄/LiFePO₄ interface, and then examined the initial charging process by introducing a Li vacancy (in the Kröger-Vink notation) into the interface. Based on the calculated results of the Li vacancy formation energies (E_V), the formation of space charge layer has been discussed.

2. Computational details

For geometry optimization and electronic structure analysis, density functional theory (DFT) was used with the PBE functional [9] implemented in CP2K [10]. Total energy only at the Γ point in a super cell approach is calculated. The hybrid Gaussian (MOLOPT DZVP) and plane-wave basis set [11] was used with the GTH pseudopotentials [12]. We set the cutoff energy of the plane-wave to 800 Ry enough to discuss the Li vacancy formation energy (E_V). The Li vacancy formation energies have been calculated by using Li metal as a reference system of Li atom. We applied +U strategy to include the electronic correlation of Fe, setting the value of the effective U to be 4.3 eV [13-16]. Although LiFePO₄ with olivine structure is anti-ferromagnetic as already confirmed theoretically and experimentally [17-19], ferromagnetic LiFePO₄ was assumed in our calculation because there is no large physical difference between anti-ferromagnetic and ferromagnetic LiFePO₄ at the DFT level [18,19].

We have used the stoichiometric Li₃PO₄ (100)/LiFePO₄ (010) coherent interface that is composed of the (1 $\times$ 3 $\times$ 2) LiFePO₄ (010) surface slab, corresponding to (LiFePO₄)₂₄, and (3 $\times$ 1 $\times$ 2) Li₃PO₄ (100) surface slab, corresponding to (Li₃PO₄)₂₄ composition as shown in Figure 1. The interface structure composed initially has an inversion symmetry with respect to Fe, P, and O atoms. Although Li atoms slightly violate the symmetry after the structural optimization, the bottom and top interface structures are similar to each other. See the reference [8] for the details.

Figure 1. Unit cell of the Li_3PO_4 (100)/ LiFePO_4 (010) coherent interface which is consisted of the $(1 \times 3 \times 2)$ LiFePO_4 (010) surface and $(3 \times 1 \times 2)$ Li_3PO_4 (100) surface slabs. Cell parameters are also given. Li ions stemmed from Li_3PO_4 and LiFePO_4 phase are depicted with green and blue balls respectively.

We estimated E_V in the $\text{Li}_3\text{PO}_4/\text{LiFePO}_4$ interface with respect to Li metal using the following equation [19];

$$E_V = [E_{\text{tot}}(V_{\text{Li}}^X) + E(\text{Li metal})] - E_{\text{tot}}. \quad (1)$$

Here, E_{tot} and $E_{\text{tot}}(V_{\text{Li}}^X)$ are the total energies of the interfaces before and after introducing one V_{Li}^X at a given site and $E(\text{Li metal})$ is the energy of Li metal.

3. Results and Discussions

3.1. Electronic structure of the Li_3PO_4 (100)/ LiFePO_4 (010) interface

At first, the electronic structure of the Li_3PO_4 (100)/ LiFePO_4 (010) interface is examined. Figure 2 shows the contour map of density of states (DOS) of the Li_3PO_4 /LiFePO₄ interface along the *b* axis that is perpendicular to the interface. The middle layers of the Li_3PO_4 and LiFePO_4 regions have almost the same local density of states (LDOS) as the respective bulk materials and thus are regarded as the bulk regions. The band gap of LiFePO_4 is estimated to be 3.7 eV from the energy difference between the valence band maximum (VBM) and the conduction band minimum (CBM) in the bulk region, both of which stem from the 3*d* orbitals of Fe atom. On the other hand, the VBM of Li_3PO_4 is mainly composed of the 2*p* orbitals of O atom and the band gap is calculated as 5.9 eV. Very close to the interface the level mixing between Li_3PO_4 and LiFePO_4 is apparent. The interface bonding between Fe in LiFePO_4 and O of PO_4 in Li_3PO_4 causes slight charge transfer from Li_3PO_4 to LiFePO_4 , while any interface level which may act as an acceptor or a donor is not formed within the band gap. From the energy difference between the VBM and CBM of Li_3PO_4 and LiFePO_4 in each bulk regions, the band offsets of the valence bands (VB) and conduction bands (CB) of Li_3PO_4 and LiFePO_4 at the interface are estimated to be 1.2 eV and 1.0 eV, respectively. This large VB offset indicates that the Li_3PO_4 electrolyte is electrochemically stable against to the LiFePO_4 electrode, that is, has a wide potential window.

Figure 2. Contour map of density of states (DOS) for beta spin electrons in the Li_3PO_4 (100)/ LiFePO_4 (010) interface along the b axis. Fermi energy of the whole system is set to zero. It is noted that the system under consideration has two interfaces at around $b=0$ and $18 \text{ \AA}$.

3.2. Li vacancy formation energies in the $\text{Li}_3\text{PO}_4/\text{LiFePO}_4$ interface

In order to give an insight into the initial stage of the charging process, we introduce V_{Li} at several sites of the $\text{Li}_3\text{PO}_4/\text{LiFePO}_4$ interface. When one V_{Li} is introduced in each bulk materials, the formation energies are calculated to be 3.59 eV and 5.27 eV, respectively, for LiFePO_4 and Li_3PO_4 (see the Supplementary Data), which correspond to the Li chemical potential relative to Li metal [19]. The large difference in the Li chemical potential between LiFePO_4 and Li_3PO_4 might be thought to hamper the Li diffusion across the $\text{Li}_3\text{PO}_4/\text{LiFePO}_4$ interface during charging and discharging processes, but this is not the case as explained below.

We introduce one V_{Li} at several sites in the $\text{Li}_3\text{PO}_4/\text{LiFePO}_4$ interface, that is, the sites in the LiFePO_4 bulk or interface region, or the sites in the Li_3PO_4 bulk or interface region, as shown in Figure 3. The V_{Li} introduction results in the separate formation of one Li ion vacancy (V_{Li}) and an electronic hole (h) in the $\text{Li}_3\text{PO}_4/\text{LiFePO}_4$ interface. Interestingly, irrespective of the position of V_{Li} , the associated h is found to be always donated to the LiFePO_4 region and oxidize Fe^{2+} into Fe^{3+} ($\text{Fe}_{\text{Fe}}^{\bullet}$) to form an acceptor level in the band gap. The calculated results of the E_V are tabulated in Table 1.

Figure 3. Initial sites of the Li vacancy (V_{Li}) introduced to the $\text{Li}_3\text{PO}_4/\text{LiFePO}_4$ interface: the bulk

B1, interface IF1, IF2 sites in the LiFePO₄ region and the bulk B2, interface IF3, IF4 sites in the Li₃PO₄ region.

Table 1. Li vacancy formation energies (E_V) relative to Li metal in the LiFePO₄ bulk and interface regions and in the Li₃PO₄ bulk and interface regions of the Li₃PO₄ (100)/LiFePO₄ (010) interface.

	LiFePO ₄ phase			Li ₃ PO ₄ phase		
Initial sites	B1	IF1	IF2	B2	IF3	IF4
E_V / eV	3.21	2.82	2.17	3.49	2.45	2.30

3.2.1. Li vacancy formation energies in the bulk region of Li₃PO₄/LiFePO₄

Figure 4 shows the contour map of density of state (DOS) in the Li₃PO₄/LiFePO₄ interface, where one is introduced at the B1 site in the bulk region of the LiFePO₄ phase. Because the Fe²⁺ atom in bulk LiFePO₄ has the octahedral coordination with its surrounding six O atoms, the 3d orbitals of Fe²⁺ split into three t_{2g} and two e_g orbitals and the electronic configuration is represented by $(t_{2g})^4(e_g)^2$. The oxidized Fe²⁺ [that is, Fe³⁺ ( )] has the electronic configuration of $(t_{2g})^3(e_g)^2$. When one is introduced in the bulk LiFePO₄ region of the Li₃PO₄/LiFePO₄ interface, as shown in Figure 4, the associated h is localized at one of the neighboring Fe²⁺ to form an unoccupied t_{2g} orbital of as an acceptor level in the band gap of LiFePO₄, as indicated by the red dotted circle. On the other hand, no change appears in the Li₃PO₄ phase. Accordingly, both the Li⁺ ion vacancy ( ) and the associated h are donated to the LiFePO₄ phase, as in bulk LiFePO₄. This implies that E_V is almost the same as that of bulk LiFePO₄. Indeed, E_V is calculated as 3.21 eV, which is close to that in bulk LiFePO₄.

Figure 4. Contour map of density of states (DOS) for beta spin electrons in the $\text{Li}_3\text{PO}_4/\text{LiFePO}_4$ interface along the b axis, when one V_{Li} is introduced at the B1 site in the bulk region of the LiFePO_4 phase. In this case, both the Li^+ ion vacancy (V_{Li}) and the electronic hole (h (Fe_{Fe})) are donated in the bulk region of the LiFePO_4 phase, as indicated by the black and red dotted circles, respectively. Fermi energy of the whole system is set to zero.

Next, we introduce one V_{Li} at the B2 site in the bulk region of the Li_3PO_4 phase in the $\text{Li}_3\text{PO}_4/\text{LiFePO}_4$ interface. Figure 5 shows the contour map of DOS in this case. When one V_{Li} is introduced in the bulk Li_3PO_4 , the associated h is also donated to the VBM of Li_3PO_4 . On the other hand, when one V_{Li} is introduced in the Li_3PO_4 phase of the $\text{Li}_3\text{PO}_4/\text{LiFePO}_4$ interface, the associated h is donated not to the VBM of the Li_3PO_4 phase but to the VBM of the LiFePO_4 phase, since the latter VBM is higher in energy than the former by the value of the VB offset. It is clearly shown in Figure 5 that the h is donated to the LiFePO_4 layer around 4 Å of the b axis to form an Fe_{Fe} acceptor level in the band gap, while the insulating property of Li_3PO_4 is maintained even after the V_{Li} introduction.

The Li vacancy formation energy (E_V) at the B2 site is calculated to be 3.49 eV, which is much smaller than E_V in Li_3PO_4 bulk, since the introduced h is transferred from the Li_3PO_4 phase to the LiFePO_4 phase in the $\text{Li}_3\text{PO}_4/\text{LiFePO}_4$ interface. It is noted that E_V of the bulk Li_3PO_4 region is

close to E_V of the bulk LiFePO_4 region (3.21 eV) in the $\text{Li}_3\text{PO}_4/\text{LiFePO}_4$ interface, although E_V of bulk Li_3PO_4 and LiFePO_4 are quite different. These results imply that the difference in E_V of bulk materials (Li_3PO_4 and LiFePO_4) arises mainly from the difference in the Fermi energy (the VBM energy). Consequently, as long as the hole (h) is donated to the LiFePO_4 phase and the Li_3PO_4 phase keeps its insulating property, the Li^+ ion vacancy (V_{Li}^+) may be located in the Li_3PO_4 or in the LiFePO_4 phases without strong preference. This suggests that the large difference in the Li chemical potential between the respective bulk materials does not cause obstacles to the Li diffusion across the $\text{Li}_3\text{PO}_4/\text{LiFePO}_4$ interface. However, the separate formation of the negatively-charged V_{Li}^- in the Li_3PO_4 phase and the positively-charged $h(\text{Fe}_{\text{Fe}}')$ in the LiFePO_4 phase results in the formation of an electrostatic dipole layer, which lifts up the electronic levels of the Li_3PO_4 phase relative to those of the LiFePO_4 phase, such as the VBM of the middle Li_3PO_4 layer is located just below the Fe_{Fe}' acceptor level in the LiFePO_4 phase, as shown in Figure 5. It is not likely that a number of V_{Li}^+ are introduced in the bulk Li_3PO_4 region, which would form a large electrostatic dipole.

Figure 5. Contour map of density of states (DOS) for beta spin electrons in the $\text{Li}_3\text{PO}_4/\text{LiFePO}_4$ interface along the b axis, when one V_{Li}^+ is introduced at the B2 site in the bulk region of the Li_3PO_4 phase. In this case, V_{Li}^+ is in the Li_3PO_4 phase while h is donated in the LiFePO_4 phase, as indicated by the dotted circles. Fermi energy of whole system is set to zero.

3.2.2. Li vacancy formation energies near the interface of $\text{Li}_3\text{PO}_4/\text{LiFePO}_4$

Here, we focus on the effects of the interface structure itself, which is different from the bulk materials. One V_{Li} is introduced near the interface region, that is, the IF1 and IF2 sites on the LiFePO_4 side and the IF3 and IF4 sites on the Li_3PO_4 side. When one V_{Li} is introduced at the IF1 site on the LiFePO_4 side, the associated h is localized at one of the neighboring Fe^{2+} to form an $\text{Fe}^{3+}(\text{Fe}_{\text{Fe}})$ acceptor level in the LiFePO_4 band gap, similar to the case of the B1 site, as shown in the DOS contour map of Figure 6. On the other hand, when one V_{Li} is introduced at the IF3 site on the Li_3PO_4 side, the associated h is donated to the LiFePO_4 side and localized on the interface Fe^{2+} ion, as shown in the DOS contour map of Figure 7.

Figure 6. Contour map of density of states (DOS) for beta spin electrons in the $\text{Li}_3\text{PO}_4/\text{LiFePO}_4$ interface along the b axis, when one V_{Li} is introduced at the IF1 site on the LiFePO_4 side of the interface. In this case, both V_{Li} and h are introduced in the interface region of the LiFePO_4 phase, as indicated by the dotted circles. Fermi energy of whole system is set to zero.

Figure 7. Contour map of density of states (DOS) for beta spin electrons in the $\text{Li}_3\text{PO}_4/\text{LiFePO}_4$ interface along the b axis, when one V_{Li} is introduced at the IF3 site. In this case, the introduced V_{Li} moves from the initial IF3 site near to the IF5 site in the Li_3PO_4 side (refer to the text and Figure 8), while the associated h appears in the LiFePO_4 side, as indicated by the dotted circles. Fermi energy of whole system is set to zero. The similar contour maps are also obtained in the cases of IF2 and IF4 (See the Supplementary Data).

Figure 8. Trajectory representation in the process of the structural reconstruction in the $\text{Li}_3\text{PO}_4/\text{LiFePO}_4$ interface when one V_{Li} is initially introduced at the IF3 site on the Li_3PO_4 side. The arrows indicated the direction of Li migration. After this reconstruction, the

introduced V_{Li} moves near to the IF5 site.

It is noted that after one V_{Li} is introduced near the interface (the IF2, IF3, and IF4 sites), large structural reconstruction occurs and as a result the introduced Li^+ ion vacancy (V_{Li}) moves far from its initial position and it becomes difficult to classify the V_{Li} site clearly. In the case of the V_{Li} introduction to the IF3 site, as a result of the structural reconstruction the introduced V_{Li} moves from the initial IF3 site near to the IF5 site, as shown in Figure 8. It is likely that V_{Li} prefers to stay near the interface. When V_{Li} is introduced near the interface, the associated h (Fe_{Fe}) is also introduced near the interface. The electrostatic dipole induced by the separate formation of the negatively-charged V_{Li} and the positively-charged h (Fe_{Fe}) is small and has negligible effects due to the short distance between them, which is clearly demonstrated in Figure 7 showing the band alignment changes slightly compared with the pristine $Li_3PO_4/LiFePO_4$ interface. The Li vacancy formation energy (E_V) is calculated to be 2.82 eV (IF1) and 2.17 eV (IF2) on the $LiFePO_4$ side and 2.45 eV (IF3) and 2.30 eV (IF4) on the Li_3PO_4 side, which are much smaller than those in the bulk regions. The small values of E_V near the interface are attributed to the large structural reconstruction near the interface induced by the V_{Li} introduction (See the Supplementary Data for the cases of the V_{Li} introduction to the IF2 and IF4 sites)

Finally, we discuss the formation of space charge layer and the resultant interface resistance in terms of the calculated results. The small values of E_V at the interface sites mean that the Li atom near the interface has smaller Li chemical potentials than in the bulk regions. Thus, these Li atoms may be extracted from the interface at a relatively lower voltage in the initial stage of charging, which seems to result in the Li depletion at the interface acting as an obstacle to the Li diffusion across the interface. However, this interface does not reach the Li depletion, because the V_{Li} introduction (that is, the Li extraction) affects the following V_{Li} introduction due to the induced structural reconstruction. In order to examine the reconstruction effect, we introduce four V_{Li} sites

simultaneously near the interface. Although the E_V values for the respective four sites are about 2.3 eV when they are introduced as a single V_{Li} , the average value of E_V for the simultaneous introduction of four V_{Li} is estimated to be 2.86 eV. This means that after some V_{Li} sites are introduced with small E_V , structural reconstruction occurs to make the interface more stable, and then the rest of the V_{Li} sites are introduced with much larger E_V of about 3.4 eV. These results suggest that although only a fraction of the Li atoms near the interface may be extracted at the initial stage of charging, the E_V raised by the structural reconstruction maintains the rest of Li atoms taking part in the ionic conduction at the $Li_3PO_4/LiFePO_4$ interface.

4. Conclusion

We have theoretically investigated the electronic structures of the $Li_3PO_4(100)/LiFePO_4(010)$ interface and examined the initial charging process by introducing V_{Li} into the interface. The estimated band offset at the interface indicates that the Li_3PO_4 electrolyte is electrochemically stable to the $LiFePO_4$ electrode. The Li vacancy formation energy (E_V) in the $LiFePO_4$ and Li_3PO_4 bulk regions of the interface are found to be almost equal. This is because irrespective of the position of the introduced V_{Li} , the associated μ is always donated to the $LiFePO_4$ region while the Li_3PO_4 region maintains its insulating properties. Although the Li atoms near the interface have smaller E_V than in the bulk regions, it is suggested that only a fraction of them may be extracted at the initial stage of charging which is not enough to result in the Li depletion and hamper the Li diffusion at the interface. These obtained results might provide useful insights into the charging process in the $Li_3PO_4/LiFePO_4$ interface.

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