



Density functional studies of olivine-type LiFePO_4 and NaFePO_4 as positive electrode materials for rechargeable lithium and sodium ion batteries



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ABSTRACT

Olivine-type LiFePO_4 is a positive electrode material for rechargeable Li ion batteries with high power density (i.e. ability of fast charge–discharge rates). However, its Na alternative, olivine-type NaFePO_4 , has a low power density as an electrode material for Na ion batteries. To understand the large difference of power density between LiFePO_4 and NaFePO_4 , their ion and electron transport properties are investigated by first-principles density functional theory (DFT). In the present DFT studies, no significant difference is observed in electronic migration energies in both bulk LiFePO_4 and NaFePO_4 . On the other hand, the migration energy of sodium ion in NaFePO_4 is 0.05 eV higher than that of lithium ion in LiFePO_4 , which may account for slow kinetics in NaFePO_4 electrode. Further studies of the phase stability and alkaline ion migration at the interfaces between the two phases of $(\text{Li}/\text{Na})\text{FePO}_4$ and FePO_4 suggest that the difference in rate performance between LiFePO_4 and NaFePO_4 is related to the formation of this interface.

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1. Introduction

Interest in olivine-type LiFePO_4 positive electrodes for rechargeable Li ion batteries has grown, because it is a cheap, abundant, and safe electrode material [1–3]. Several studies have reported the fast charge–discharge capability and high power density of LiFePO_4 derivative materials, which also exhibit stable cycling at a high current rate [4–8]. Thus, LiFePO_4 is expected to be used in batteries for hybrid and electric vehicles and portable devices. However, the limited availability of and access to Li reserves have led to economic uncertainty and speculation about the future use of Li ion batteries, particularly for large batteries [9–12]. Therefore, research has intensively focused on Na ion batteries, which can offer a potential cost advantage because of the vast supply of Na. In this respect, the alternative Na electrode material, olivine-type NaFePO_4 , has been studied experimentally and theoretically [13–23]. However, olivine-type NaFePO_4 is not thermodynamically stable, and conventional solid-state reactions result in the formation of a maricite-type structure [15,24]. Thus, the electrochemical ion exchange method is used to synthesize olivine-type NaFePO_4 compounds [13,15,18]. NaFePO_4 has been prepared by electrochemical

ion exchange of Li ions in LiFePO_4 with Na ions, and the rate performance of the same electrode composite sheet was compared. Therefore, the effects of morphology and the micro- or mesopore structure of the cathode composite were eliminated. The slow kinetics in NaFePO_4 may be caused by diffusion-driven resistance, namely the ion and electron transport properties, in solid-state electrodes. In particular, the ionic radius of Na^+ is larger than that of Li^+ , which could increase the migration energy because of the repulsion arising from electron overlap between surrounding ions during hopping [25,26]. Zhu et al. reported that the diffusion coefficient of Na^+ is 1–2 orders of magnitude lower than that of Li^+ in the olivine-type FePO_4 structure [18]. To understand the difference in the rate performance between LiFePO_4 and NaFePO_4 arising from ion and electron migration, we performed first-principles density functional theory (DFT) calculations for both compounds.

2. Computational method

All the first-principles DFT calculations were performed with the Vienna Ab Initio Simulation Package [27,28] using the modified Perdew–Burke–Ernzerhof generalized gradient approximation (PBEsol-GGA) [29,30] and the projector-augmented wave (PAW) method [31]. Onsite Coulomb correction (GGA + U) was included to describe the localized electronic states of Fe 3d in mixed-valence rare earth metals.

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U was set to 4.0 eV for the Fe 3d states, according to the literature [32, 33]. A spin polarization calculation was used. A kinetic cutoff energy of 500 eV, and $5 \times 5 \times 3$ k -point meshes in the $A\text{FePO}_4$ unit cell (28 atoms, $A = \text{Li}$ or Na) were found by a convergence test (<3 meV/ $A\text{FePO}_4$). Because the band gaps of both compounds were underestimated, which is typical of the GGA + U functional [34], we used the Heyd–Scuseria–Ernzerhof (HSE06) hybrid functional to estimate the band gaps, and we calculated the intercalation voltages of LiFePO_4 and NaFePO_4 from the total energies of two end compositions before and after alkaline ion removal and metallic Li and Na. The details are described in Refs. [35,36].

The energy profiles for the localized hole (polaron) hopping to the nearest neighbor Fe site in the $A\text{FePO}_4$ cell were calculated by adapting the method used in Ref. [37]. First, the total energies and relaxed internal configurations of the local energy minima, q_i and q_f , in which a localized electron was positioned at one of the adjacent Fe ions, were calculated. Because the polaron hopping energy corresponds to the sequential variation of the local lattice distortion between the two configurations of q_i and q_f , it was assumed that the migration path could be linearized from the two configurations. The total energy calculation was performed for each intermediate configuration. The nudged elastic band (NEB) method [38] was used to investigate the minimum energy pathways of the alkaline ion jumps from one lattice position to adjacent sites. Both the hole and ion migration calculations were performed with $2 \times 2 \times 1$ (112 atoms) supercells ($2 \times 2 \times 2$ k -point meshes). An on-site Coulombic interaction, U term, was not included in the NEB calculations, because the numerous configurational degrees of freedoms of the hole arrangements along the ion migration path cause technical difficulties for convergence, as reported in the literatures [39,40].

3. Results and discussion

Table 1 lists the lattice parameters and intercalation voltages between $A\text{FePO}_4$ and FePO_4 calculated by the GGA + U and HSE06 methods. The present computational and previous experimental/computational lattice parameters and voltages agreed well. The voltage of $\text{LiFePO}_4/\text{FePO}_4$ was 0.41 V higher than that of $\text{NaFePO}_4/\text{FePO}_4$, which is slightly higher than the difference of 0.33 V in experimental anodic half-cell potential between Li^+/Li and Na^+/Na . Therefore, the lattice energies were slightly less stable for olivine-type NaFePO_4 compared with LiFePO_4 [19].

Fig. 1(a) and (b) shows the partial density of states (PDOS) around the Fermi level for olivine-type LiFePO_4 and NaFePO_4 , respectively, calculated by the HSE06 functional. The electronic configuration of both compounds is similar. The localized Fe 3d bands form a valence band maximum and conduction band minimum, and the band gaps are larger than 3.8 eV in both compounds. Therefore, the intrinsic band conduction of electrons is negligible at room temperature because of the localization and wide band gap. Electronic conduction in LiFePO_4 mainly arises from localized electron/hole (polaron) hopping [19]. Polarons are created by the redox reaction of $\text{Fe}^{2+/3+}$ to maintain charge neutrality during electrochemical Li^+ or Na^+ removal (uptake). Fig. 2(a) shows the calculated energy profiles for localized hole (Fe^{3+}) jumps of ~ 0.2 eV for both compounds. The polaron migration energies are much smaller than the band gaps, and thus polaron migration is

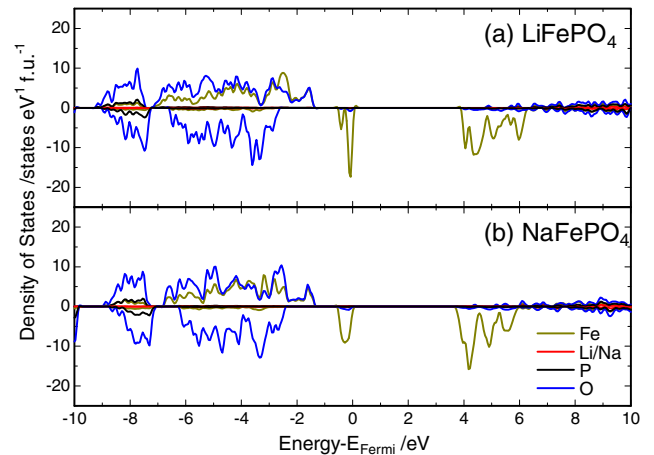


Fig. 1. Partial density of states (PDOS) for (a) LiFePO_4 and (b) NaFePO_4 . PDOS is aligned so that the Fermi energy is zero.

the dominant electron conduction mechanism. The similarity of the polaron migration energies of the two compounds indicates that the difference in rate performance does not stem from polaronic migration.

Alkali ion migration is another factor affecting the rate performance in batteries. NEB calculations were performed to evaluate the migration energies of alkali ions in LiFePO_4 and NaFePO_4 . The GGA functional was used to avoid the effect of complicated polaron interactions. Fig. 3 shows the migration trajectory of Na^+ hopping in the NaFePO_4 bulk structure, which is similar to that of Li^+ in LiFePO_4 (not shown). Li or Na ions at the octahedral site jump to the neighboring site via the tetrahedral vacancy site along the $\langle 010 \rangle$ direction, forming one-dimensional pathway as reported in previous reports [6,7,41]. The migration energy profiles are shown in Fig. 2(b), where the energy maximum is located at the center of migration path (tetrahedral vacancy). The migration energies are 0.29 and 0.35 eV in LiFePO_4 and NaFePO_4 , respectively, which is consistent with previously reported values [19]. The migration energy of Na^+ is slightly larger than that of Li^+ , which may arise from the size effect of the larger ionic radius of 6-coordinate Na^+ (1.02 Å) compared with Li^+ (0.76 Å). According to Ref. [6], the diffusion coefficient, D , can be expressed by migration energy, E_m , as follows,

$$D = a^2 \nu^* \exp\left(\frac{-E_m}{k_B T}\right) \quad (1)$$

where a , ν^* , k_B and T correspond to hopping distance, attempt frequency, Boltzmann constant, and absolute temperature, respectively. Therefore, the diffusion coefficient of Li, D_{Li} , reaches around 10-fold that of Na, D_{Na} , at room temperature from $D_{\text{Li}}/D_{\text{Na}} = \exp(0.06 \text{ eV}/k_B T)$. Thus, above difference may account for the observed slow kinetics in Na insertion/removal reaction into/from $\text{Na}_{1-x}\text{FePO}_4$ electrode. Note that the diffusion distance, $\langle l \rangle$, is proportional to the square root of the diffusion coefficient, \sqrt{D} , according to random walk theory ($D = \langle l^2 \rangle / (2t)$ for one dimensional diffusion [41]), the difference in migration distance is only a factor of 2.2 ($\sim \sqrt{10}$). In this respect, the effect of difference in diffusion coefficient between the two compounds (Fig. 2(b)) may be small, if the particle size is small. Further study, such as finite element method (FEM), is required to estimate quantitatively the impact of migration energy difference between two compounds. In addition, the particle size effect is needed to evaluate experimentally to consider the blocking effect of anti-site defects in the one-dimensional diffusion tunnel as reported in Ref. [41].

It has been reported that a major difference in the charge–discharge mechanism between compounds is the compositional range of the miscibility gap [13,42]. A wide miscibility gap, which allows two phases

Table 1

Computational voltages in the present study, and reported computational and experimental voltages for $A\text{FePO}_4/\text{FePO}_4$ ($A = \text{Li}$ or Na).

	Voltage calculated in this study	Reported voltage	
	Computational (V)	Computational (V)	Experimental (V)
$\text{LiFePO}_4/\text{FePO}_4$	3.39 (HSE06)	3.45 (GGA + U) [19]	3.5 [1]
	3.52 (GGA + U)		
$\text{NaFePO}_4/\text{FePO}_4$	2.98 (HSE06)	3.08 (GGA + U) [19]	~ 3 [15]
	2.90 (GGA + U)		

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