Effect of Sodium Substitution into $LiFePO_4$ Cathode Material: A First Principles Studies

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Abstract. The demand for Lithium-ion batteries has increased drastically with the introduction of electric vehicles and wide use of portable devices. The scarcity of lithium sources will soon increase the prices of the battery. Sodium has been widely studied as an alternative to lithium as they have almost similar chemical properties. Lithium iron phosphate is a widely used cathode material for rechargeable batteries. In this work, the effect of sodium substitution into $LiFePO_4$ has been studied. Using computational approaches, the structural and electronic properties of sodium-$LiFePO_4$ have been calculated by means of density functional theory using GGA-PBE + U method. Upon substitution, the lattice parameter of $LiFePO_4$ undergoes change, resulting in volume expansion. In terms of electronic properties, no significant change has been seen as the band gap of sodium-$LiFePO_4$ is almost the same as pure $LiFePO_4$, suggesting the electronic conductivity would remain the same. However, there is a significant reduction in ionic conductivity, as the sodium ion requires higher energy to migrate.

Keywords: Sodium-ion, cathode material, $LiFePO_4$, migration energy, Lithium-ion battery.

Introduction

In 2021, The International Energy Agency (IEA) published its roadmap for zero-carbon emissions by 2050 [1], resulting in an increase in the global initiative toward using electric vehicles. Meanwhile, the Euro has targeted about 30 million electric vehicles on the road to reduce fossil fuel dependency by 2030 [2]. For this to be achieved, good energy storage must be relied on. To date, lithium-ion batteries have been recognized as the most promising energy storage and have been used in most electric vehicles. However, due to the increasing demand for lithium-ion batteries, the scarcity of lithium sources has urged researchers to find an alternative to lithium [3]. The most compatible replacement for lithium is sodium because their chemical properties are almost similar. Sodium-ion batteries also can be operated in a similar mechanism to lithium-ion batteries. Moreover, the abundance of sodium in the earth's crust has made sodium-ion batteries relatively lower costs and suitable for large-scale energy storage devices[4].

Proper sodium battery candidates have been intensively studying for many years such as NASICON $Na_3V_2(PO4)_3$ [5], $NaFePO_4$ [6], $Na_xCoFe(CN)_6$ [7], and $Na_xFe[Fe(CN)_6$ [8]. Among the iron-base phosphate, $NaFePO_4$ possesses the highest theoretical capacity of 154 mAh g^{-1}, making it an attractive cathode material for sodium-ion batteries. However, the olivine $NaFePO_4$ is not favored with sodium analog [9]. To stabilize the structure, Wang et al. have substituted the $NaFePO_4$ with the amount of Lithium and found that the structure should be more stable at >25% of Lithium content [6].

Therefore, in this study, the sodium ion is substituted into $LiFePO_4$ (LFP) cathode material by replacing half of the lithium-ion. The studies are performed using computational code based on density functional theory (DFT). The structural, electronic properties, and electrochemical properties of sodium-LFP were calculated and presented in this work. There is a slight increase in the volume of cells with sodium incorporated. The band gap value indicates that the electronic conductivity of sodium-$LiFePO_4$ (Na-LFP) is almost unchanged compared to pristine LFP. However, the migration energy of sodium atoms is larger compared to lithium, which can cause lower ionic conductivity.

Computational Details

In this work, all the calculations were performed using CASTEP [10] computer code implemented in Material Studio Software based on the density function theory (DFT). The generalized gradient approximation (GGA)[11] exchange-correlation functional is used. As iron is naturally magnetic, spin-polarization is considered. To model valence-electron interactions with Li $1s^1 2s^2$, Na $2s^2\ 2p^6\ 3s^1$, O $2s^2 2p^4$, P $3s^2 3p^3$, Fe $3d^6 4s^2$ as valence electron configuration, the ultrasoft pseudopotential was considered. GGA+U method is included with U = 4.3 eV of an effective Hubbard U parameter as the energy gap is always underestimated using GGA-PBE functional alone. This method describes the localized electronic states of Fe 3d in the compound. The following value of Hubbard U has been used repetitively in previous work as it can reproduce the experimental band gap [12–14]. This calculation employed the plane wave cut-off energy of 500 eV and Monkhorost-Pack scheme k-points of 5 × 6 × 7 for Brillouin zone integrations. The ferromagnetic configuration is adopted based on point energy calculation (the most stable). Half of the lithium atoms are replaced with sodium to investigate the effect of sodium substitution. Broyden–Fletcher–Goldfarb–Shanno (BFGS) algorithm is used for the geometry optimization with the following convergence condition of self-consistent-field (SCF): the energy change per atom is 5×10^{-6} eV, the maximum force is 0.01 eV/A, the maximum stress is 0.02 GPa, and the maximum displacement of atoms is 0.0005 A. Finally, the lattice parameters, band gaps, and Li-ion migration are computationally obtained to describe the electrochemical properties of these compounds.

Result and Discussion

Table 1 shows the calculated lattice parameter of LFP and Na-LFP compared to the experimental work. Upon sodium doping, the lattice parameter and volume of Na-LFP undergoes expansion where the volume increases up to 5.67 %. This situation is attributed to the size of sodium ions being bigger than lithium ions. Based on Shannon et al. [15] database, the sodium ion for four coordination is 0.99 Å of ionic radii compared to lithium-ion, which is 0.59 Å. This expansion of lattice can cause unstable conditions toward the lattice framework and reduce the cycle life of the battery. However, compared to a fully sodiated structure, half sodiated structure ($Li_{0.5}Na_{0.5}FePO_4$) has lower volume expansion and should be more stable. Based on previous work, lithium was purposely introduced to replace the sodium content inside the $NaFePO_4$. It is found that, for lithium content greater than 25%, the structure will have better stability than a fully sodiated structure ($NaFePO_4$) [6]. Doping with transition metals such as Mn could also help to stabilize the structure more [16].

Table 1: The calculated lattice parameter of $LiFePO_4$ and Sodium-LFP compared with other theoretical and experimental work.

Structures	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)	Volume (Å)	Ref.
$LiFePO_4$	10.349	6.031	4.772	90	90	90	294.719	*This work
$LiFePO_4$	10.380	6.050	4.750	-	-	-	298.30	*[17]
$LiFePO_4$	10.332	6.010	4.692	90	90	90	291.400	[18]
$Li_{0.5}Na_{0.5}FePO_4$	10.454	6.126	4.864	89.996	91.089	89.999	311.43	*This work
$NaFePO_4$	10.405	6.223	4.949	-	-	-	319.93	[9]
$NaFePO_4$	9.07	6.90	5.08	-	-	-	318.26	*[19]

*Theoretical work

Fig. 1 shows the total Density of States of Na-LFP generated using GGA+U. Without incorporating the Hubbard U parameter, the band gap of Na-LFP is nearly described with metallic character. Therefore, including the Hubbard U parameter in the calculation is important, especially when dealing with transition metal compounds. Based on Fig. 1, the band gap of Na-LFP (3.53 eV) is almost the same as its pure counterpart, which is 3.7 eV. Based on previous work on $NaFePO_4$, Nakayama et al.[20] reported that the electronic properties of both $LiFePO_4$ and $NaFePO_4$ are identical. With this wide band gap, insulating properties are expected to impede the self-generation of electrons or holes, resulting in low electrical conductivity of this cathode material. Therefore, to solve this problem, doping this material with small amounts of metal/non-metal [21–23] elements or coating [24,25] it with a carbon layer or both methods still need to be done to overcome this conductivity issue.

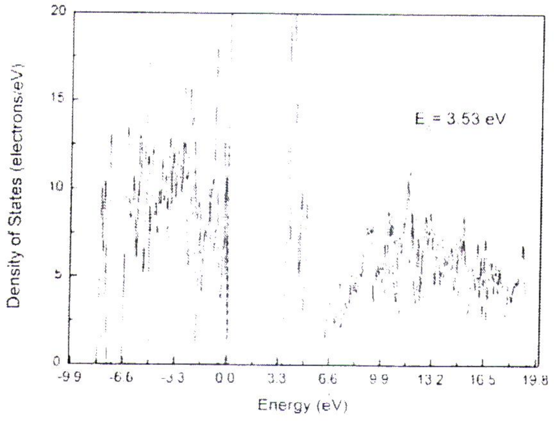

Fig. 1 Total Density of States (DOS) of Na-LFP generated using GGA + U method.

Ion mobility and kinetic inside the cathode material are crucial concerning the rate of charge/discharge in the battery. Low migration energy is desirable for high-rate cathode material. Fig. 2 shows sodium and lithium migration energy inside the cathode material. Sodium ion takes 0.987 eV energy meanwhile lithium takes 0.758 eV. The result for lithium is similar to the previous report [14]. Based on the result, the sodium ion required higher energy than lithium ion. As the sodium ion is larger than lithium, moving through the one-dimensional channel is harder as it needs to encounter the electrostatic force inside the same size channel compared to lithium ion. This will lead to slower kinetic and lower discharge and charge rates. Although the cell has been expanded, larger spaces are required for it to move easily. Based on this result, pure $LiFePO_4$ is unable to handle sodium perfectly. Alternative structures like Prussian blue cathode material [26] with open large structures are more suitable for sodium ions as charge carriers.

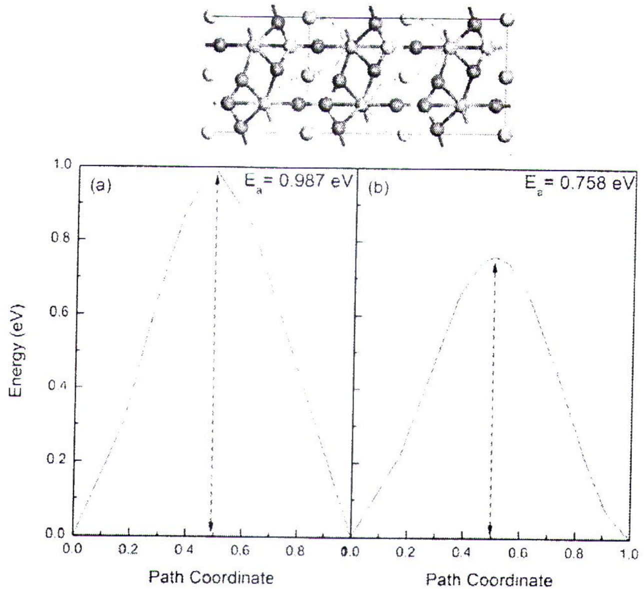

Fig. 2 The calculated migration energy of (a) sodium ion and (b) lithium ion in the LFP cathode material. Sodium atom, lithium atom, oxygen atom, iron atom, and phosphate atom are in green, purple, red, grey, and pink colour. The green dotted line showed the migration pathway in the cathode material.

Conclusion

Density functional theory has been employed in CASTEP computer code to calculate the structural, electronic, and electrochemical properties of half sodiated $LiFePO_4$. The lattice parameter and volume undergo expansion owning to a larger sodium ion radius compared to lithium ion. In terms of electronic properties, no significant change has been observed for half-sodiated $LiFePO_4$ compared to its pure counterpart, which remains insulated in nature due to its wide band gap property. For migration energy, sodium requires higher energy to migrate which can slow the kinetics thus reducing the rate capability of the batteries. It is recommended that the half-sodiated $LiFePO_4$ is modified by doping with transition metal/non-metal or carbon coated to improve the electrochemical performance of the cathode material.

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