



Short communication

Looking beyond single electron extraction in cathode materials for lithium ion batteries



Anish Suresh Sankhe, Sumit Saxena*, Priya Shrivastava, Shobha Shukla

Nanostructures Engineering and Modeling Laboratory, Department of Metallurgical Engineering and Materials Science, Indian Institute of Technology Bombay, Mumbai, MH 400076, India

HIGHLIGHTS

- Explore possibility of extracting >1 Li^+ by Na^+ substitution in cathode materials.
- Substitution by Na^+ widens the path for easier extraction and provides stability.
- Crystal symmetry is preserved even after complete delithiation process.
- Electronic, energetics, structural phase properties suggest Na^+ substitution helps.

ARTICLE INFO

Article history:

Received 1 October 2014
 Received in revised form
 13 December 2014
 Accepted 10 January 2015
 Available online 10 January 2015

Keywords:

Lithium ion battery
 Density functional theory
 Electronic structure
 Silicates

ABSTRACT

One of the challenges in enhancing the performance of Lithium ion batteries for stable energy storage is looking beyond extraction of single electron per formula unit of cathode material during the delithiation without phase change of the material. We have investigated lithium ferrous silicate by partial substitution of lithium by sodium atoms using density functional theory to achieve this. Our calculations have suggested that the substitution of lithium with sodium in controlled amounts is just sufficient to provide structural and phase stability during delithiation process. The larger size of sodium atom assists in easier extraction of lithium ions by providing wider pathways. These studies suggest the possibility of extracting more than one Li-ion per formula unit making this a promising cathode material for use in Li-ion battery applications.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

The decreasing level of fossil fuels and an escalating demand for energy globally, has resulted in urgent need not only to generate energy but also to store it using rechargeable batteries. This will enable in making available energy generated especially from non-conventional energy sources, as a sustainable option for long term use. A battery is a transducer that converts chemical energy into electrical and vice versa *via* redox reaction. Even though the batteries are inherently simple conceptually, their overall development has progressed at much slower pace due to lack of suitable electrode materials and electrolytes [1]. Although commercialized by Sony as early as 1991, lithium ion batteries are still objects of intense research leaving much scope for their improvement.

One of the key features of lithium ion battery is that the lithium ion participates at both electrodes, being reversibly inserted and extracted from the electrode material [2], with concomitant addition or removal of electrons. Thus the cathode in a rechargeable lithium ion battery must be stable over long cycling time, low cost, good ionic as well as electron conductor and environmentally benign [3]. Although several materials such as LiNiO_2 [4], LiCoO_2 [5], LiMnO_2 [6], LiFePO_4 [7] have been explored, these were however dismissed on one or more accounts related to safety, environmental hazards, economic feasibility, cyclability etc. In the recent past, orthosilicates (Li_2MSiO_4 , $\text{M} = \text{Transition Metal}$) have attracted considerable attention as desirable cathode materials due to their high capacities. Studies have shown that orthosilicates in principle can deliver theoretical capacities of around 330 mAh g^{-1} owing to possibility of more than one electron exchange per formula unit [8–11]. But practically such high capacities have not been achieved due to their poor intrinsic electronic properties, structural and phase stability [12,13]. The use of iron as transition metal

* Corresponding author.

E-mail address: sumit.saxena@iitb.ac.in (S. Saxena).

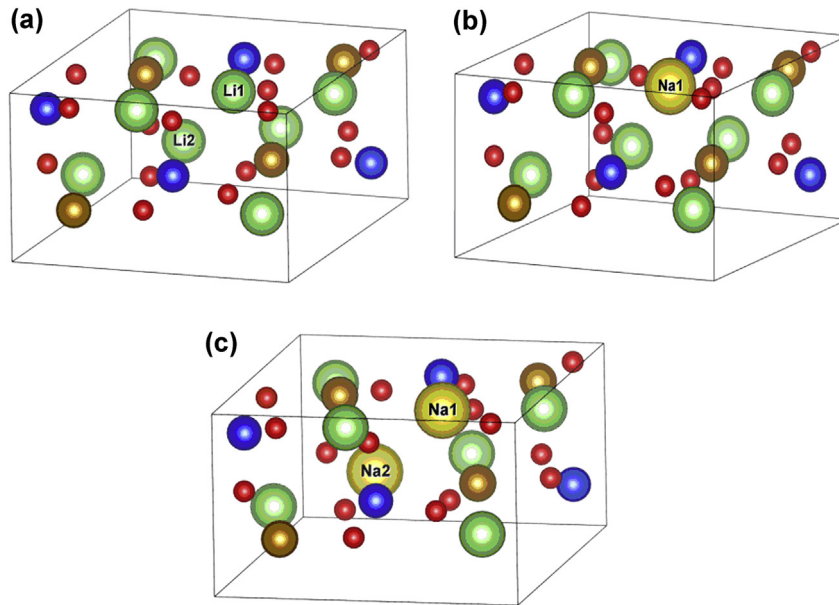


Fig. 1. Optimized crystal structure of $\text{Li}_{2-x}\text{Na}_x\text{FeSiO}_4$ for (a) $x = 0$, (b) $x = 0.25$ and (c) $x = 0.5$. Green, Red, Gold, Blue and Yellow balls represent lithium, oxygen, iron, silicon and sodium atoms respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

among orthosilicates make them significantly cheaper and more environmentally favored technology platform along with better electronic properties. $\text{Li}_2\text{FeSiO}_4$ depicts impressive electrochemical performance and complex polymorphism [9,14–20]. Although $\text{Li}_2\text{FeSiO}_4$ in $\text{Pmn}2_1$ symmetry offers good electronic properties, their relative theoretical conductivity is somewhat lower and reversibility along with cycling performance is not good [8]. In 2008 Nishimura et al. proposed a different structure with the $\text{P}2_1$ symmetry using high-resolution synchrotron XRD [17] which shows much better properties [21].

Intensive research is being pursued to improve the performance of these orthosilicates by implementing techniques such as coating with carbon composite, doping with hetero atoms and reducing grain size [10,14,22–26] etc. The practical electrochemical performance of lithium ion battery has been quite unsatisfactory [27,28] as at the most one of the lithium ions per formula unit can be removed from the parent material of the family in $\text{Li}_2\text{FeSiO}_4$ due to $\text{Fe}^{2+} \leftrightarrow \text{Fe}^{3+}$ active redox couple. A major breakthrough in current Li-ion battery technology is expected to arise by being able to overcome the current intrinsic limitation of extracting more than one lithium ion per formula unit of cathode material. Our goal here is to probe the viability of new iron silicate based active cathode material by using density functional theory (DFT) to overcome this current intrinsic limitation of single Li-ion extraction. We have investigated the substitution of Li atoms with Na atoms and analyzed the effects on the structural stabilities of $\text{Li}_2\text{FeSiO}_4$, bonding character and electronic properties. These investigations are expected to provide significant lead and catalyze research in pursuit of extracting more lithium ions per formula unit to enhance the performance of Li ion batteries.

First principles calculations using projected augmented wave (PAW) method within the density functional theory as instrumented in Vienna Ab Initio Simulation Package (VASP) were performed [29]. Plane-wave basis set with cutoff energy of 500 eV was used. The convergence thresholds were set as 10^{-5} eV in energy and 0.01 eV/Å in force. K-points mesh of $4 \times 8 \times 4$ was generated using Monkhorst and Pack grid scheme. The exchange – correlation energy was treated with the spin -polarized local density approximation (LDA) using parameterization of Ceperley and Alder (CA). The calculations were repeated with generalized gradient approach using Perdew, Burke and Ernzerhof (PBE) functional. Furthermore the localization of 3d electrons were taken care of by using GGA + U approach with an effective value of $U' = U - J = 4.3$ eV [30]. All calculations were performed using supercell of $\text{Li}_{2-x}\text{Na}_x\text{FeSiO}_4$ consisting of 32 atoms with $\text{P}2_1$ symmetry.

2. Results and discussion

$\text{Li}_2\text{FeSiO}_4$ in $\text{P}2_1$ symmetry consists of FeO_4 and SiO_4 tetrahedrons taking periodically opposite directions with each SiO_4 tetrahedron sharing its four corners with four neighboring FeO_4 tetrahedra and vice versa [11]. The structure of sodium substituted $\text{Li}_{2-x}\text{Na}_x\text{FeSiO}_4$ (x being, 0, 0.25 and 0.5) shown in Fig. 1 were obtained by substituting appropriate Li atoms in the supercell and relaxing the structure completely. Further increased substitution of Na is expected to influence the theoretical capacity and core properties of this material rendering it incapable to act as an efficient cathode material for Li-ion batteries due to reduced concentration of lithium ions. These may however be utilized for use as electrode materials for sodium ion batteries [31]. Optimized

Table 1
Optimized lattice parameters and equilibrium volumes for $\text{Li}_{2-x}\text{Na}_x\text{FeSiO}_4$ ($x = 0, 0.25, 0.5$) obtained using LDA (GGA + U) compared with experimentally reported data in Ref. [11]. V represents the volume of the supercell while ΔV represent the increase in volume.

Material	a (Å)	b (Å)	c (Å)	V (Å ³)	% ΔV	α (°)	β (°)	γ (°)
$\text{Li}_2\text{FeSiO}_4$	8.06961 (8.2824)	4.95123 (5.08230)	8.07407 (8.27557)	318.48 (343.76)	–	90.0244 (90.0296)	99.1554 (99.3988)	90.0468 (90.0403)
$\text{Li}_2\text{FeSiO}_4$ [17]	8.22898	5.02002	8.23335	335.74	–		99.2027	
$\text{Li}_{1.75}\text{Na}_{0.25}\text{FeSiO}_4$	8.13480 (8.35205)	4.98653 (5.16952)	8.12292 (8.33812)	325.96 (356.04)	2.34 (3.57)	89.8739 (89.9347)	98.3998 (98.5039)	89.6189 (89.6773)
$\text{Li}_{1.5}\text{Na}_{0.5}\text{FeSiO}_4$	8.18791 (8.4290)	5.03808 (5.17851)	8.18453 (8.3901)	334.57 (362.78)	5.05 (5.53)	90.0112 (90.0101)	97.7152 (97.8601)	90.0147 (90.0196)

Download English Version:

<https://daneshyari.com/en/article/7733889>

Download Persian Version:

<https://daneshyari.com/article/7733889>

[Daneshyari.com](https://daneshyari.com)