Looking Beyond Single Electron Extraction in Cathode Materials for Lithium Ion Batteries

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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.

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 , M=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 330mAhg^{-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 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 4x8x4 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 $P2_1$ symmetry.

Results and Discussion

$\text{Li}_2\text{FeSiO}_4$ in P2_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 Figure 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].

Each lithium atom in $\text{Li}_2\text{FeSiO}_4$ is bonded to its 4 neighboring oxygen atom. Table 2 shows that the average Li-O bond length for $\text{Li}_{2-x}\text{Na}_x\text{FeSiO}_4$ for $x=0.25$ and 0.5 is greater than in that the pure $\text{Li}_2\text{FeSiO}_4$ compound. A larger Li-O bond length implies weaker Li-O interactions and a wider pathway for Li ion diffusion. The average Fe-O and Si-O bond lengths however remain almost similar suggesting that their bonding nature remains unchanged. Substitution of Li atoms by Na in $\text{Li}_2\text{FeSiO}_4$ leads to volume expansion similar to that observed in $\text{Li}_2\text{CoSiO}_4$ [32], the phase change of this material during the delithiation process is not known.

The electronic properties can be used to investigate the feasibility of the materials to be used as electrode material for lithium ion batteries. In order to truly explore the potential of $\text{Li}_{2-x}\text{Na}_x\text{FeSiO}_4$ as potential cathode materials, spin polarized total density of states (DOS) were calculated using DFT+U method. The GGA+U method provides a more accurate treatment of Coulomb correlations by pushing the majority and minority spin towards the lower and higher

energy levels there by opening up band gaps in materials which otherwise would be characterized as metals using normal DFT calculations.

The DOS of both pure and sodium substituted $\text{Li}_2\text{FeSiO}_4$ shows a sharp peak just below the Fermi level in the spin down channel. Further analysis of the spin orbital decomposed density of states (PDOS) suggests that the major contribution to this peak can be traced back to the contribution arising from the d_{yz} , d_{xz} and d_{xy} orbitals. Since the Fe atom in $\text{Li}_{2-x}\text{Na}_x\text{FeSiO}_4$ ($x=0, 0.5$) occupies the central site of oxygen tetrahedral, it can be concluded that the electron in this spin down state belongs to the higher energy t_2 states. Most of the other contribution to the DOS further away from the Fermi level due to the d electrons arises mostly due to the stabilized e states. The projected density of states at the site of sodium substitution suggests no significant change in the electronic contribution of s and p orbital. However, strong hybridization between 3d electronic states of Fe and 2p electronic states of oxygen is observed. The electronic properties of Na substituted $\text{Li}_2\text{FeSiO}_4$ is found to improve over pristine $\text{Li}_2\text{FeSiO}_4$. These observations are consistent for both LDA and GGA calculations.

The suitability of these materials as cathode material can be estimated by performing delithiation studies. Lithium atoms were extracted step by step for $\text{Li}_{2-x}\text{Na}_x\text{FeSiO}_4$ by removing 1, 1.25 and 1.5 atoms per formula unit to understand the delithiation properties. A comparison of total energies has been plotted in Figure 3. It is observed that the delithiation of $\text{Li}_{2-x}\text{Na}_x\text{FeSiO}_4$ leads to increase in total energy of the system suggesting the formation of unstable structure, however no change in phase is observed. It is important to note that complete delithiation of $\text{Li}_2\text{FeSiO}_4$ results in sudden decrease in volume which is associated with change of phase of pristine $\text{Li}_2\text{FeSiO}_4$. This abrupt change in volume and phase in $\text{Li}_{1.5}\text{Na}_{0.5}\text{FeSiO}_4$ is not observed

suggesting that sodium substitution help in stabilizing the crystal structure and maintain its symmetry.

Conclusions

In summary, the $P2_1$ symmetrical pure $\text{Li}_2\text{FeSiO}_4$, $\text{Li}_{1.5}\text{Na}_{0.5}\text{FeSiO}_4$ and $\text{Li}_{1.75}\text{Na}_{0.25}\text{FeSiO}_4$ have been studied using density functional theory. Effects of sodium substitution on the electronic and structural properties of $\text{Li}_2\text{FeSiO}_4$ are presented. The lattice parameters undergo expansion on substitution of lithium by sodium atoms in pure $\text{Li}_2\text{FeSiO}_4$. This substitution provides wider routes for the extraction and insertion of Li ions during discharging and charging processes. Thus wider diffusion pathways and better electronic properties along with structural and phase stability during complete delithiation suggest that $\text{Li}_{1.5}\text{Na}_{0.5}\text{FeSiO}_4$ in $P2_1$ symmetry is a promising cathode material for extracting more than one Li ion per formula unit.

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Tables

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 (°)
Li₂FeSiO₄	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)
Li₂FeSiO₄ [17]	8.22898	5.02002	8.23335	335.74	-		99.2027	
Li_{1.75}Na_{0.25}FeSiO₄	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)
Li_{1.5}Na_{0.5}FeSiO₄	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)

Table 2: Average bond length of Li – O, Fe – O, and Si – O in Å for $\text{Li}_{2-x}\text{Na}_x\text{FeSiO}_4$ where $x=0, 0.25$ and 0.5 calculated using LDA (GGA+U).

Compound	Li – O	Fe – O	Si – O
Li ₂ FeSiO ₄ (LDA/GGA+U)	1.922/1.9749	1.967/2.0381	1.628/1.6556
Li _{1.75} Na _{0.25} FeSiO ₄ (LDA/GGA+U)	1.930/2.0015	1.968/2.0363	1.630/1.6567
Li _{1.5} Na _{0.5} FeSiO ₄ (LDA/GGA+U)	1.941/2.0026	1.967/2.0404	1.630/1.6576

Figure Captions

Figure 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.

Figure 2: Total density of states calculated for $\text{Li}_{2-x}\text{Na}_x\text{FeSiO}_4$ for (a) $x=0$ (b) $x=0.5$ were obtained using GGA+U ($U-J = 4.3$). The red graph represents spin-up DOS while the blue graph represents spin-down DOS

Figure 3: Comparison of total energy (for 4 formula units) for delithiation of pure (purple and red) and sodium substituted (green and blue) $\text{Li}_2\text{FeSiO}_4$ obtained using LDA (dot and square) and GGA+U (inverted and upright triangles). The horizontal axis represents the no. of lithium atoms removed per formula unit. The black line is just a guideline for the eye.

(a)

(b)