Ab-initio modelling of new cathode material for Li-ion battery based on the Ti substituted Li$_2$Fe(SO$_4$)$_2$
Ab-initio Modelling of New Cathode Material for Li-ion Battery based on the Ti Substituted Li$_2$Fe(SO$_4$)$_2$

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Abstract. This work demonstrates the battery-related properties of Li$_2$Fe(SO$_4$)$_2$ and its Fe site Ti substituted derivatives (Li$_2$Ti$_{0.5}$Fe$_{0.5}$(SO$_4$)$_2$ and Li$_2$Ti(SO$_4$)$_2$) using ab-initio calculations. The calculated voltage profile of all these systems clearly indicates the increase of voltage with delithiation. Even though the average voltage values of Ti-substituted systems gradually changes with the Ti concentration, they are still in the range of requirement for a good cathode material. In most of the cases, Ti substitutions increase the specific capacity and energy density of Li$_2$Fe(SO$_4$)$_2$. The negative enthalpy of formation implies that all the considered systems are thermodynamically stable. These results indicate that Ti-substituted Li$_2$Fe(SO$_4$)$_2$ could be a potential cathode material for rechargeable Li-ion batteries.

INTRODUCTION

Lithium-ion battery is one of the cutting-edge energy storage technologies due to its low-cost, low toxicity, high theoretical capacity, excellent cycling stability and thermal stability as well as good lifespan. Increasing the energy density of a cathode material is a great challenge in finding higher efficiency lithium ion batteries. The cathode material we have chosen to work is Li$_2$Fe(SO$_4$)$_2$ because it has the theoretical capacity of 102 mA h g$^{-1}$ and a high potential of 3.83 V vs. Li/Li$^+$ for the Fe$^{2+}$/Fe$^{3+}$ redox couple[1]. Also it is environmentally benign, safe, and inexpensive as well as naturally abundant. Recent developments on Li$_2$Fe(SO$_4$)$_2$ system holds promise to use it as a cathode material in Li-ion battery applications [2]. The main aim of this work is to improve the energy density and specific capacity of Li$_2$Fe(SO$_4$)$_2$ by substituting other transition metals in Fe site. In most of the chemical environment Fe is in $+2$ and $+3$ oxidation state. Therefore, only one Li ion is available for charging-discharging kinetics in Li$_2$Fe(SO$_4$)$_2$. Since Ti is cost effective, light weight, low toxic and abundant as well as it can exist in $+4$ oxidation states also, we focus on Ti substitution in the Fe site of Li$_2$Fe(SO$_4$)$_2$. We used two different Ti substitution concentration and the corresponding compositions are Li$_2$Ti$_{0.5}$Fe$_{0.5}$(SO$_4$)$_2$ and Li$_2$Ti(SO$_4$)$_2$. As Ti can have oxidation states from $+2$ to $+4$, its substitution can lead to the extraction of more Li ions from the Li$_2$Fe(SO$_4$)$_2$ during redox reaction and thereby increase the gravimetric energy density.

COMPUTATIONAL DETAILS

All calculations were done using the Vienna Ab-initio Simulation Package (VASP) [3], which is based on density functional theory (DFT). We used the Perdew-Burke-Ernzerhof (PBE) exchange and correlation functional within GGA+U level, with the projector augmented wave (PAW) method. The wave function energy cut-off was set...
to 700 eV for Li$_2$Fe(SO$_4$)$_2$. Accurate Brillouin-zone integrations are carried out using Monkhorst-Pack $k$ point mesh of 4x4x2 for Li$_2$Fe(SO$_4$)$_2$.

**RESULTS AND DISCUSSION**

In Table 1 we have listed the optimized lattice parameters for all the compounds (Li$_2$Fe(SO$_4$)$_2$, Li$_2$Fe$_5$Ti$_3$(SO$_4$)$_2$ and Li$_2$Ti(SO$_4$)$_2$) considered for the present study and are crystallizes in the orthorhombic structure with the space group Pcab. The optimized equilibrium structural parameters and ground state volume for Li$_2$Fe(SO$_4$)$_2$ are in good agreement with previous report.[4] The calculated equilibrium lattice parameters and volumes for Li$_2$Fe$_5$Ti$_3$(SO$_4$)$_2$ and Li$_2$Ti(SO$_4$)$_2$ are gradually increase with increasing the Ti concentration (see Table 1).

![FIGURE 1. The optimized ground state crystal structures of (a) Li$_2$Fe(SO$_4$)$_2$ and (b) Li$_2$Fe$_5$Ti$_3$(SO$_4$)$_2$.](image)

<table>
<thead>
<tr>
<th>Composition</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>V (Å$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li$_2$Fe(SO$_4$)$_2$</td>
<td>9.287</td>
<td>9.374</td>
<td>13.823</td>
<td>1203.47</td>
</tr>
<tr>
<td></td>
<td>9.295$^a$</td>
<td>9.401$^a$</td>
<td>13.858$^a$</td>
<td>1211.17$^a$</td>
</tr>
<tr>
<td>Li$<em>2$Ti$</em>{0.5}$Fe$_{0.5}$(SO$_4$)$_2$</td>
<td>9.343</td>
<td>9.407</td>
<td>13.882</td>
<td>1219.98</td>
</tr>
<tr>
<td>Li$_2$Ti(SO$_4$)$_2$</td>
<td>9.355</td>
<td>9.454</td>
<td>13.880</td>
<td>1227.67</td>
</tr>
</tbody>
</table>

$^a$Ref[5]

The calculated formation enthalpy value for Li$_2$Fe(SO$_4$)$_2$ given in Table 2 is in agreement with corresponding literature value. The small difference in the presently calculated enthalpy of formation value with that from literature value is due to the fact that we have done 0K calculations whereas, literature values are available at room temperature. There is no literature heat of formation value available for all the other substituted systems to compare with because none of these compounds are synthesized or done the computation yet. All the selected compositions represent negative formation enthalpy values and hence all of them are thermodynamically stable. Further, the above-reported values clearly show that when the concentration of Ti at Fe sites increases the enthalpy of formation value decreases. One can also note that the removal of Fe from Li$_2$Fe$_{0.25}$Ti$_{0.75}$(SO$_4$)$_2$ and its substitution by Ti atoms leads to a comparatively steep reduction in stability.
The intercalation voltage is calculated using the equation.

\[
V = \frac{E(Li_{x2}M(SO_4)_2) + n \cdot E(Li) - E(Li_{x1}M(SO_4)_2)}{n}
\]  

\( \cdots \cdots \ ) (1)

TABLE 2. Calculated enthalpy of formation for pure Li₂Fe(SO₄)₂ and Ti substituted Li₂Fe(SO₄)₂ composition.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Enthalpy of Formation(eV)</th>
<th>Enthalpy of Formation(eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li₂Fe(SO₄)₂</td>
<td>-25.966</td>
<td>-29.159^a</td>
</tr>
<tr>
<td>Li₂Ti₀.₅Fe₀.₅(SO₄)₂</td>
<td>-27.396</td>
<td>-</td>
</tr>
<tr>
<td>Li₂Ti(SO₄)₂</td>
<td>-28.472</td>
<td>-</td>
</tr>
</tbody>
</table>

^Ref[5]

with \( x_1 > x_2 \). In the above equation, \( V \) corresponds to the voltage, \( E(Li_{x2}M(SO_4)_2) \), \( E(Li_{x1}M(SO_4)_2) \) and \( E(Li) \) are the energy of the corresponding systems and \( n \) is the number of Li atoms transferred during the intercalation reaction. From equation (1) it may be noted that the voltage value is directly dependent on the formation energy of delithiated phases. The voltage profile was calculated by gradually removing the relevant Li atoms from the parent compound and optimized the structure to its minimum energy configuration. Even though, we could obtain the minimum energy configurations for the delithiated phases; one cannot neglect the probability of phase transition and thereby some voltage variation during Li-ion extraction.

FIGURE 2. The calculated voltage profile for (a) Li₂Fe(SO₄)₂, (b) Li₂Fe₀.₅Ti₀.₅(SO₄)₂, and (c) Li₂Ti(SO₄)₂.

The intercalation voltage value of 4.1V for Li₂Fe(SO₄)₂ obtained from present calculation is in good agreement with previous report of 3.99 V from DFT calculations [1]. From the voltage profile in figure 2 one can see that the voltage grows with the delithiation process. This is a common behaviour in battery electrode materials. As a function of lithiation process, the voltage profile is varying smoothly in LiₓFe(SO₄)₂, LiₓFe₀.₅Ti₀.₅(SO₄)₂, and Li₂Ti(SO₄)₂ indicating no abrupt changes in the crystal structure. In figure 2(b), the abnormal change in voltage at the Li concentration 0.75 and 1.25 may be due to configurational or the valence change of the metal ion. Whereas, there is no voltage decline for the Ti fully substituted systems (figure 2(c)), and hence the voltage profile is continuously smooth with lithiation process. From figure 2 the parent and partial Ti substituted systems provide maximum voltage of about 5 V at fully charged states, whereas fully Ti substituted at Fe sites system leads to the maximum voltage of about 5 V at fully charged states. It is to be noted that the currently available electrolyte does not withstand a voltage higher than 5 V. Hence, the Ti substitution in Li₂Fe(SO₄)₂ considerably improved the battery properties of Li₂Fe(SO₄)₂ to use it for practical applications.
The average voltage, specific capacities, specific energy, charge density, and energy density were calculated and are tabulated in Table 3. The specific capacity of Li$_2$Fe(SO$_4$)$_2$ is gradually increasing with increasing the Ti substitution. The Ti substituted Li$_2$Fe(SO$_4$)$_2$ illustrate higher energy density than parent compound. All these properties of Ti-substituted Li$_2$Fe(SO$_4$)$_2$ cathode make these materials as a promising cathode materials for future generation Li-ion batteries.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Average Voltage (V)</th>
<th>Specific Capacity (Ah/kg)</th>
<th>Specific Energy (Wh/kg)</th>
<th>Charge Density (Ah/mL)</th>
<th>Energy Density (Wh/mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li$_2$Fe(SO$_4$)$_2$</td>
<td>4.1</td>
<td>102</td>
<td>418</td>
<td>44.370</td>
<td>182</td>
</tr>
<tr>
<td>Li$<em>2$Ti$</em>{0.5}$Fe$_{0.5}$(SO$_4$)$_2$</td>
<td>3.1</td>
<td>156</td>
<td>484</td>
<td>66.821</td>
<td>207</td>
</tr>
<tr>
<td>Li$_2$Ti(SO$_4$)$_2$</td>
<td>2.07</td>
<td>212</td>
<td>439</td>
<td>89.464</td>
<td>185</td>
</tr>
</tbody>
</table>

CONCLUSION

The average voltage, specific capacity, specific energy, charge density, and energy density for pure and Ti substituted Li$_2$Fe(SO$_4$)$_2$ were calculated using DFT calculations. We have calculated the battery properties such as specific energy, intercalation voltage and enthalpy of formation for pure and the Ti substituted Li$_2$Fe(SO$_4$)$_2$. We found that the specific capacity and energy density of Li$_2$Fe(SO$_4$)$_2$ are gradually increasing with increasing the Ti substitution. The calculated enthalpy of formation of Ti-substituted compositions showed more negative values than the parent compound indicating that all of them are thermodynamically stable and one can experimentally synthesize these compounds. All the calculated battery related properties of Ti-substituted Li$_2$Fe(SO$_4$)$_2$ suggest that these systems are promising cathode materials for higher efficiency Li-ion batteries.

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