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Ab-initio Based Thermodynamic Study on α-NaMnO₂ for Na-ion Battery Applications

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Abstract. In this work, the thermodynamic properties of the monoclinic NaMnO₂ is analyzed with density functional theory based calculations. Cluster expansion methods are used to find the minimum formation energy configurations at different concentrations of Na removal. This material shows a strong Na vacancy ordering during the extraction of Na from the host structure. Several ground state configurations as a function of Na composition are predicted by the cluster expansion method. The thermodynamic intercalation potential of the electrode is calculated using Monte Carlo simulation. The stability of the cathode material at higher temperatures are also analyzed.

INTRODUCTION

There has been considerable attention paid to identify novel cathode materials for Na ion battery as the increasing awareness among battery researchers about the depleting Li resources and the consequent increase of material cost for Li ion batteries. Layered monoclinic NaMnO₂ is found to be an interesting cathode material for Na ion batteries. NaMnO₂ has several polymorphs and among these the monoclinic α-NaMnO₂ is found to be the most stable ground state configuration¹. The α-NaMnO₂ has an intercalating structure suitable for the insertion/removal of Na-ions. In order to understand the Na intercalation process, we have made the thermodynamic study of α-NaMnO₂ using the results based on density functional theory calculations. The Na intercalation properties are analyzed from the voltage profile curves plotted using the Monte Carlo method implemented in the Cluster Assisted Statistical Method (CASM) code. The voltage profiles are plotted for 0 K, and 300K in order to analyze the electrochemical properties of this material at different temperatures. For the analysis of the Na intercalation, possible structural configurations are generated for each Na concentrations using the supercell method and the formation energy for all the configurations are cluster expanded to identify the ground state configurations. These ground state configurations are used to compute the voltage profiles.

COMPUTATIONAL DETAILS

All the DFT total energies of monoclinic - NaMnO₂ were calculated using VASP (Vienna Ab initio simulation Package) code. The exchange-correlation functional in the generalized gradient approximation as given by Perdew, Burke, and Ernzerhof (GGA-PBE)² is used to calculate the total energies. In order to account for the correlation effects of electrons in the d orbitals of the transition metal Mn, Hubbard U parameters are included. The U value used is 3.68 for Mn³. The plane wave cut off energy was set to 800 eV and the 2×2×2 k-point grid was used for all the calculations. Spin polarized calculations are performed for finding the energies of all the configurations.

For identifying the possible Na vacancy configurations for each concentration of Na, supercells of size up to 6 units were used. The total number of enumerated configurations were 654 and out of which total energies for 64 configurations were calculated using DFT. The calculated total energies are used to parameterize the cluster expansion using the CASM software package to predict the thermodynamic properties. Monte Carlo simulations that
are implemented in the CASM software package is used to perform the calculations of voltage profiles at finite
temperatures. The finite temperature calculations were done using the statistical method of semi grand canonical
ensemble methods. The metropolis and low temperature expansion algorithms are used to find the variation of
voltage with respect to the change in concentration of Na at the host structure.

STRUCTURAL DETAILS

For the present study we have used the monoclinic form of NaMnO$_2$ with space group as C2/m as the primary
structure. Figure 1 shows the optimized crystal structure of $\alpha$-NaMnO$_2$.

![Figure 1: Crystal structure of $\alpha$-NaMnO$_2$. Pink balls represent Mn atoms, green balls represents O atoms
and the red ball represent Na atom.]

The layered structure of this material can be seen with Mn atoms surrounded by oxygen atoms forming
polyhedra of octahedral coordination as shown in pink color. The optimized structural parameters are shown in table
1, with other experimental and theoretical values for comparison.

<table>
<thead>
<tr>
<th>TABLE 1</th>
<th>Optimized structural parameters for $\alpha$-NaMnO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compound</td>
<td>Lattice parameters (Å)</td>
</tr>
<tr>
<td>NaMnO$_2$</td>
<td>a, b, c</td>
</tr>
<tr>
<td></td>
<td>2.928, 3.227, 5.613</td>
</tr>
<tr>
<td></td>
<td>2.924, 3.232, 5.620$^*$</td>
</tr>
</tbody>
</table>

RESULTS AND DISCUSSION

Different possible Na-vacancy configurations for each Na concentrations are generated using CASM code and out of
which total energy for randomly selected 64 configurations are computed using DFT method. The DFT computed
total energies of these configurations are used to parametrize the cluster expansion to find the formation energies of
all the configurations possible for Na-vacancy ordering. The formation energies for all the compositions are plotted
against the Na concentration obtained from CASM method and from density functional total energy calculations in
figure 2a and 2b, respectively to understand the charging/discharging profile of this cathode material. The formation
energy of all the compounds calculated as a function of Na concentration $x$ shown in the figure 2 are defined as:

$$E_f(x) = E(Na_xMnO_2) - xE(NaMnO_2) - (1 - x)E(MnO_2)$$
Where $E(\text{Na}_x\text{MnO}_2)$ is the total energy of a particular Na vacancy ordering at concentration $x$ in $\text{Na}_x\text{MnO}_2$, $E(\text{NaMnO}_2)$ is the energy of completely sodiated configuration. $E(\text{MnO}_2)$ is the total energy of completely desodiated configuration. All the formation energies are calculated per unit cell.

**FIGURE 2.** (a) The formation energy as a function of Na concentration in Na$_x$MnO$_2$ where blue lines are the lowest energy configuration obtained from DFT calculations and the red line is from cluster expansion method. (b) The formation energy estimated from the total energies from DFT for 64 configurations along with the extrapolated values for the other configurations based on cluster expansion method.

Figure (2a) shows the formation energy calculated using the DFT and formation energies that are found from cluster expansion method. Cluster expansion predicts the ground state energy for several concentrations of Na including $x = 0.5$, $x = 0.33$, $x = 0.75$, $x = 0.80$ and $x = 0.83$. The accuracy of cluster expansion method can be observed from the figure as overlapping blue circle and the red dot representing the cluster expanded formation energy and the DFT computed energy respectively.

The figure 2(b) shows that the cluster expansion method predicts a strong tendency for Na vacancy ordering at various intermediate stoichiometric compositions of Na in the host structure. The formation energies for all the configurations are negative indicating that Na$_x$MnO$_2$ is thermodynamically stable. This means that at low temperatures, at a particular Na concentration $x$, the stable phase will be either a stoichiometric compound in which the Na and vacancy are ordered on the host superlattice, or a mixture of ordered stoichiometric compounds. At higher temperatures, the possibility is that the ordered phase will shift to a disordered phase. It can also be noted that the ground state configuration for the Na vacancy ordering happens at the concentration of $x = 0.5$ in Na$_x$MnO$_2$ with fairly large difference in energy with the next lowest energy configuration. This figure also reveals that at $x = 0.67$, the lowest energy configuration has energy that is very close to the ground state configuration energy. These show the likelihood of emergence of a solid solution between these two concentrations at higher temperatures as the difference in energy between these two are very small. But these may be partially disturbed by the occurrence of a higher energy configuration at $x = 0.60$ which lies between these two low energy configurations.

*Voltage profiles*

The voltage profiles at finite temperature are calculated using Monte Carlo method implemented in CASM code. Figure 3 shows the voltage profiles at different temperature with varying concentration of Na in Na$_x$MnO$_2$ as in the process of discharging. Monte Carlo simulation gives the chemical potential as a function of concentration of Na at finite temperature. The equilibrium potential of an electrochemical cell depends on the chemical potential difference of the sodium in anode and cathode materials as
If the anode potential is taken as the standard potential for metallic sodium, then the cell potential is the negative of the chemical potential in cathode which can be directly obtained by Monte Carlo method.

\[ V(x) = -\frac{\mu_{Na\text{ cathode}}(x) - \mu_{Na\text{ anode}}(x)}{e} \]

The voltage profile curves follow the same trends in all the figures indicates the stability of the material at higher temperatures. In all the voltage profiles, sharp voltage steps occur at the concentration \( x = 0.33 \) shows a strong ordering of Na vacancy indicating a first order phase transition at this composition. Also it should be noted that the maximum sodium that can be removed is only 65\%, and above that concentration the voltage reduces drastically. Though the maximum voltage can be attained in \( \alpha \)-NaMnO\(_2\) is low, the possibility of extraction of a constant voltage from this material adds to the benefit of this as a cathode material for Na-ion battery.

**CONCLUSION**

Thermodynamics of Na intercalation in the compound NaMnO\(_2\) is analyzed using statistical methods like cluster expansion and Monte Carlo simulation. The material \( \alpha \)-NaMnO\(_2\) shows a strong tendency for Na vacancy ordering and exhibits many stable configurations during the extraction of Na from the host structure. The electrode potential is well below the stability window of the electrolyte. Also it is found that the material is highly stable at higher temperatures suggesting its usefulness to use as a cathode material for Naion batteries.

**ACKNOWLEDGMENTS**

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