Structural properties of P2 and O2-type layered lithium manganese oxides as potential coating materials

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Abstract. Surface coatings have been reported to improve the performance of cathode materials by altering the surface chemistry or providing a physical protective layer. There is currently a challenge of obtaining the most suitable coating materials between the O2 and P2 type structure for coating the O3-type cathode material to mitigate the structural degradation that occurs during cycling. The density functional theory was used to investigate the structural and electronic properties of these materials in a quest to monitor their stability upon their usage as coating materials for O3-Li₂MnO₃. The partial density of states of the O2 and P2 bulk materials and O2 and P2 materials with vacancies indicated that the electron contribution at the fermi level was due to the p state of oxygen and the d state of manganese. Furthermore, the electronic band structures showed that the materials are metallic, with a band gap of zero. The P2 and O2-type cathode materials have been known to offer high energy density and excellent cycling stability while the P2 has been found to not only enhance the reversibility and air/thermal stability of other cathodes but also improve their electrochemical kinetics and reduce the charge transfer resistance.

1 Introduction

Lithium-ion batteries have been the predominant choice of energy storage systems for portable electronic devices and electric vehicles in the last few decades. The battery is associated with high energy density and long cycle life [1]. As such, the development of electrode materials with high capacity, high-rate capability, and excellent cycling stability is urgently needed to engage with high energy density LIBs. The O3-type layered metal oxide (Li₂MnO₃) cathode material has a potential for application in large-scale energy storage systems such as electric power grid and electric vehicles because it has been shown to exhibit a high specific capacity and high energy density [2]. However, structural transformation occurs during charge and discharge accompanied by the migration of the transition metal from the cathode material into the electrolyte [3]. The cathode experiences capacity fading due to the interaction with the electrolyte leading to a short battery lifespan [4].
The Li₂MnO₃ with an O₃-type structure is one of the most attractive lithium manganese oxides due to its structure and electrochemical behaviour. Initially, the O₃ type Li₂MnO₃ was thought to be electrochemically inert for lithium insertion and extraction between 2.0V and 4.4V in its microcrystalline form due to the presence of Mn⁴⁺ ion which cannot be oxidized to enable extraction of Li⁺ ion. However, the electrochemical activity of this compound has been reported to be based on oxygen removal, Li⁺, -H⁺ ion exchange and the deficit of oxygen which introduces Mn³⁺ and not by Mn⁴⁺ oxidation, reversible and accompanied by migration of Mn ion which hinders the overall cycling process. As such, the loss of essential elements from the cathode material can be potentially curbed by coating it [5].

The use of basic doping and coating as a way of enhancing lithium-ion batteries has ignited interest in most extensively used cathode materials. This has led to enhanced Li-ion penetration, ionic mobility, electric conductivity, and cyclability, as well as reduced capacity fading as compared to typical parent materials [6]. Surface coating has been shown to improve cathode materials' rate capability, thermal stability, and capacity retention in energy storage systems [7]. One material that can potentially be employed as a coating material is the O₂-type layered structure as it has been reported to display higher reversible capacity and excellent structure stability than an O₃-type (LiMnO₂) since the O₂-type stacking (ABAC) can be preserved upon cycling, whereas O₃-type layered structure (R3-M) converts to a spinel phase (Fd-3m) [8]. The robust structure stability might benefit from the fact that the O₂-type structure restricts the movements of transition metals within the Li layer, which promotes the reversibility of the cation migration and thereby suppresses the formation of spinel phase upon cycling. Competitively, the P₂-type structure is also a promising material owing to its high energy density, high volumetric capacity, excellent Na ion conductivity, ease of synthesis, and good stability [9]. On this basis, this work will study in detail the structural and electronic properties of both the P₂ and O₂-type materials to determine the most stable material to utilize as a coating material for the O₃-type cathode material.

2 Methodology

All first principle calculations were carried out using density functional theory (DFT) formalism as implemented in the Cambridge Serial Total Energy Package (CASTEP) code [10]. In the CASTEP code, the ultrasoft pseudopotential which allows for density functional theory calculations to be performed with greater computational efficiency [11] and the generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) [12] parameterization was used as the exchange correlation functional. The P₂ NaMnO₂ bulk structure, P₂ vacancy 1 and P₂ vacancy 2 were optimized with k-points 6x6x1 and cut-off energy of 600eV for P₂ NaMnO₂ and 500eV for P₂ Vacancies 1 and 2. The O₂ LiMnO₂ bulk structure was optimized with k-points 6x6x1 and cut-off energy of 500eV while the O₂ Vacancies 1 and 2 were optimized with k-points 6x6x6 and cut-off energy of 500eV.

3 Results and discussions

3.1 Crystal structures

Lattice parameters describe the unit lengths (a, b, and c) along each crystallographic axis and the angles between those axes. The triclinic lattice geometry is characterized by the
absence of any equal sides and 90° angles within its unit cell. A triclinic lattice has been selected such that its internal angles are either acute or obtuse. The crystal system under consideration exhibits minimal symmetry and necessitates specification by way of three lattice constants (a, b, c) and three angles (α, β, γ). Figures 1 and 2 show the triclinic structures of the P2 and O2 materials. The calculated lattice parameters are shown in table 1. The lattice parameters of the bulk materials were found to be a = 2.933Å, b = 2.933Å, and c = 10.868Å for NaMnO2 and a = 2.932Å, b = 2.932Å, and c = 10.867Å for LiMnO2. The P2 vacancy 1 and 2 were found to have the same lattice parameters a = 2.896Å, b = 2.890Å, and c = 10.888Å. Similarly, the O2 vacancy 1 and 2 have lattice parameters a = 2.772Å, b =2.770Å, and c = 10.254Å.

![Fig 1](image)

**Fig 1.** The structures for (a) O2-LiMnO2, (b) O2 Vacancy 1-Li0.69MnO2, and (c) O2 Vacancy 2-Li0.69MnO2.
Table 1. Calculated lattice parameters and volume for the P2 and O2 type materials.

<table>
<thead>
<tr>
<th>Structure</th>
<th>Lattice Parameters (Å)</th>
<th>Volume (Å³)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>a</td>
<td>b</td>
</tr>
<tr>
<td>NaMnO₂</td>
<td>2.933</td>
<td>2.933</td>
</tr>
<tr>
<td>P2 Vacancy 1-Na₀.₆₉MnO₂</td>
<td>2.896</td>
<td>2.890</td>
</tr>
<tr>
<td>P2 Vacancy 2- Na₀.₆₉MnO₂</td>
<td>2.896</td>
<td>2.890</td>
</tr>
<tr>
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<td>2.895</td>
</tr>
<tr>
<td>LiMnO₂</td>
<td>2.932</td>
<td>2.932</td>
</tr>
<tr>
<td>O2 Vacancy 1-Li₀.₆₉MnO₂</td>
<td>2.772</td>
<td>2.770</td>
</tr>
<tr>
<td>O2 Vacancy 2-Li₀.₆₉MnO₂</td>
<td>2.772</td>
<td>2.770</td>
</tr>
<tr>
<td>O2-Liₙ[Li₀.₄Mn₃/₄]O₂</td>
<td>2.842</td>
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</tr>
</tbody>
</table>

Fig 2. The structures for (a) O2-LiMnO₂, (b) O2 Vacancy 1-Li₀.₆₉MnO₂, and (c) O2 Vacancy 2-Li₀.₆₉MnO₂.
3.2 The total and partial density of states

The density of states (DOS) describes the probability of electron distribution in the energy spectrum while the partials density of states (PDOS) is the relative contribution of a particular atom or orbital to the total density of states. The partial and total density of states calculations were done with GGA approximations for the P2-NaMnO₂ bulk, P2 vacancy 1 and 2, O₂-LiMnO₂ bulk, and O₂ vacancy 1 and 2. Figures 3 and 4 show the PDOS of the materials. The PDOS of the P2 type materials in figure 3 is attributed to by the p state of oxygen and the d state of manganese. Furthermore, the PDOS of the O₂ type materials in figure 4 shows that the PDOS is accredited to by the p state of oxygen and the d state of manganese. Moreover, the electron contribution at the fermi level for all the materials is due to the p state of oxygen and the d state of manganese.

Figure 3. The partial and total density of states (PDOS) for (a) P2-NaMnO₂, (b) P2 Vacancy 1-Na₀.₆₉MnO₂, and (c) P2 Vacancy 2-Na₀.₆₉MnO₂ materials respectively in a spin polarized (low-spin) for antiferromagnetic spin configuration.
Figure 4. The partial and total density of states (PDOS) for (a) O2 Li$_{0.69}$MnO$_2$, (b) O2 vacancy 1-Li$_{0.69}$MnO$_2$ and O2 vacancy 2-Li$_{0.69}$MnO$_2$ materials respectively in a spin polarized (low-spin) for antiferromagnetic spin configuration.

3.3 Band structures

In solid-state physics, the electronic band structure of a solid describes the range of energy levels that electrons may have within it, as well as the ranges of energy that they may not have [15] Figures 5-10 shows the electronic band structures for the materials P2-NaMnO$_2$ bulk, P2 vacancy 1 and 2, O2-LiMnO$_2$ bulk, and O2 vacancy 1 and 2. The band structures were calculated using the CASTEP code. The band structures illustrated band gaps of zero; which is an indication that the materials are metallic, further confirming that the materials are excellent conductors.
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In solid-state physics, the electronic band structure of a solid describes the range of energy levels that electrons may have within it, as well as the ranges of energy that they may not have. Figure 3-8 shows the electronic band structures for the materials P2 - NaMnO$_2$ bulk, P2 vacancy 1 and 2, O2 - LiMnO$_2$ bulk, and O2 vacancy 1 and 2. The band structures were calculated using the CASTEP code. The band structures illustrated band gaps of zero; which is an indication that the materials are metallic, further confirming that the materials are excellent conductors.

Fig 5. The electronic band structure for NaMnO$_2$ bulk.

Fig 6. The electronic band structure for P2 vacancy 1 Na$_{0.69}$MnO$_2$. 
Fig 7. The electronic band structure for P2 vacancy 2 Na$_{0.69}$MnO$_2$.

Fig 8. The electronic band structure for LiMnO$_2$ bulk.
Fig 9. The electronic band structure for O2 vacancy 1 Li$_{0.69}$MnO$_2$.

Fig 10. The electronic band structure for O2 vacancy 2 Li$_{0.69}$MnO$_2$. 


4 Equations and mathematics conclusions

The structural and electronic properties were successfully investigated using the CASTEP ultrasoft pseudopotentials and the generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE). The results of the P2 and O2 structures with vacancies illustrated consistency, confirming that the position at which the vacancy is made has no effect on the properties of the materials. The lattice parameters were in good agreement with the ones available in literature, and the total density of states of the different materials illustrated that O2-Li0.69MnO2 vacancies 1 and 2 to be the most stable materials, with the least electron contribution at the fermi level; and the electronic band structures indicated that the materials are metallic, with a band gap of zero. Moreover, the O2-Li0.69MnO2 vacancies 1 and 2 were found to be the most stable and the best suitable materials for coating the O3 type cathode material.

References