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Theoretical investigations of Li^+ and Co^{3+} positions for layered LiCoO_2 lithium ion battery cathode material using first principle method

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Abstract. There are a few structures available for the layered LiCoO_2 cathode materials, with the metals in different atomic positions. In this study, first principles calculations based on density functional theory were used to evaluate two LiCoO_2 structures with different Li^+ and Co^{3+} atomic positions. The calculation were conducted using local density approximation and by comparing the total energy of both LiCoO_2 hexagonal $R\text{-}3m$ structure, Li^+ has more tendency for being in the 3a Wyckoff position instead of 3b. The calculated band structures of each LiCoO_2 structures were also presented in this paper.

Keywords: First Principle Method, Wyckoff position, LiCoO_2

INTRODUCTION

Lithium ion battery materials have been widely studied due to the success of the Li-ion battery as an energy device [1-3]. One of the most common cathode materials for rechargeable lithium ion batteries is lithium cobalt oxide LiCoO_2 [4-6]. The layered LiCoO_2 structure has hexagonal symmetry and belongs to the space group $R\text{-}3m$. However, with this particular structure, there are two possible positions for the metal ions (Li^+) and the transition metal ions (Co^{3+}) to occupy, that is, the 3a and 3b Wyckoff positions. The question is that, which position can give a more stable structure? There are many hexagonal structures available in the Inorganic Crystal Structure Database (ICSD) with Li^+ and Co^{3+} ions occupying different positions in the hexagonal crystal structure. It is important to study the specific positions of ions in LiCoO_2 in order to understand the performance of the cathode material with respect to the specific positions of the Li^+ and Co^{3+} ions.

This work will examine which atomic configurations will result in a more stable and viable structure via first principle calculations within the density functional theory framework. The result of the total energy for both structure are compared to determine the most stable structure of LiCoO_2 .

COMPUTATIONAL METHODS

All calculations presented were performed using first-principle DFT via Cambridge Serial Total Energy Package (CASTEP) code [7] with generalized gradient approximation (GGA) (Perdew-Burke-Ernzerhof (PBE)) functions [8]. Ultrasoft pseudopotential [9] was used to describe the electron-ion

interaction and Li ($2s^1$), Co ($3d^7, 4s^2$) and O ($2s^2, 2p^6$) were treated as the valence electron of the LiCoO_2 . The plane-wave basis set for LiCoO_2 was set at 540 eV for the energy cut-off and $8 \times 8 \times 8$ for the k-point [10]. The optimized structure done by Andriyevsky et al were used in these calculations as given in Table 1. Two atomic positions are considered. One with Li at the 3a Wyckoff position and Co at the 3b Wyckoff position and the second consideration with the positions reversed and see which configuration will give a more stable total energy value.

RESULTS AND DISCUSSIONS

Figure 1 shows the 3D visualization of the two hexagonal layered LiCoO_2 with space group of $R\bar{3}m$ that is used in this study. In Fig.1(a), the Li^+ occupy the 3a Wyckoff position and Co^{3+} occupy the 3b Wyckoff position and we can see that a form of layered Co-O and Li in the [001] direction is generated. Three layers of Co-O and Li^+ form in a single cell of LiCoO_2 and the center of this structure is the Co-O layer. On the other hand, in Fig.1(b), the 3a Wyckoff position were occupied by Co^{3+} and the 3b Wyckoff position were occupied by the Li^+ . The same number of Co-O layers and Li^+ layers form but in this arrangement, the center of this single cell structure is the Li^+ layer. The structure of Fig.1(a) and Fig.1(b) are referred to as Li3a and Li3b respectively.

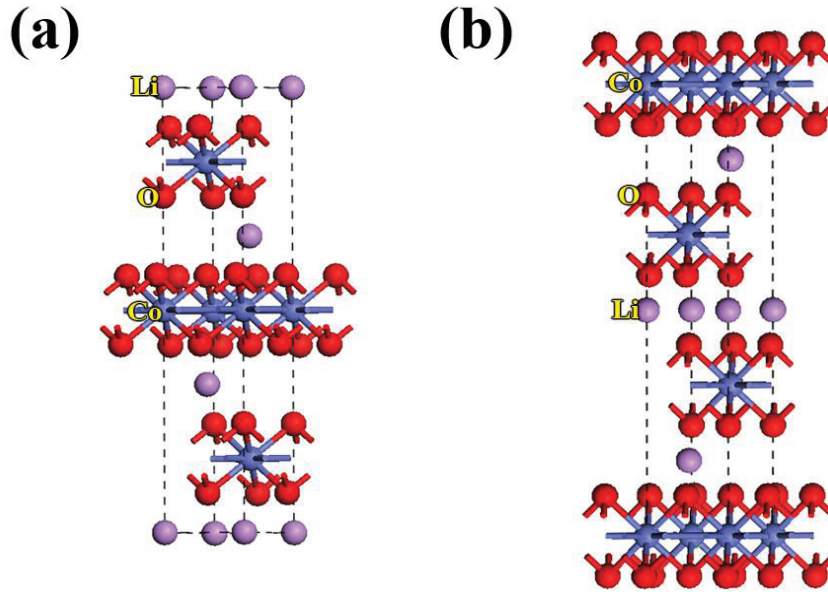


FIGURE 1. Crystal structure of (a) LiCoO_2 with Li^+ at Wyckoff 3a position and Co^{3+} at Wyckoff 3b position and (b) LiCoO_2 with Li^+ at Wyckoff 3b position and Co^{3+} at Wyckoff 3a position.

The total energy calculated for Li3a and Li3b are -6324.4 eV and -6322.3 eV respectively. It can be seen that Li3a have a lower total energy compared to the Li3b suggesting that Li3a has a more stable structure as compared to Li3b. The difference is about 0.02%. The structure of layered LiCoO_2 is prone to have Li^+ in the 3a Wyckoff position as compared to the 3b Wyckoff position since it required less energy to form

The calculated band structure of Li3a and Li3b is presented in Fig.2. For Li3a, the band structure has an indirect band gap of 1.126 eV and Li3b also have an indirect band gap but the value is 0.804 eV. The experimental value of LiCoO_2 band gap varies from 1.7 eV – 2.7 eV [11-13] and from our calculations, Li3a band structure exhibit a band gap much nearer to the experimental value. Thus the Li3a structure experimental results support a more stable LiCoO_2 layered structure. Although the Li3a band gap of 1.126 eV is still lower than the published experimental values, it nevertheless demonstrates that Li3a ionic configuration is more stable than Li3b ionic configuration of $R\bar{3}m$ crystal structure.

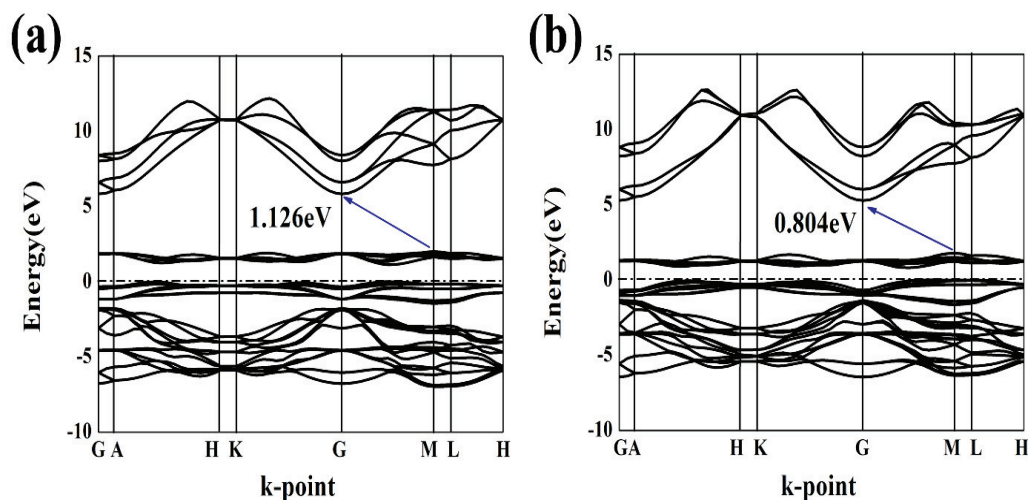


FIGURE 2. Band structure of (a) Li3a and (b) Li3b calculated using GGA PBE for the exchange correlation.

TABLE 1. The crystal input for LiCoO₂. The lattice parameters used in this structure were obtained from the literature [13].

Samples	Element	Wyckoff position	Cartesian coordinate			Lattice parameter (Å)	
			<i>x</i>	<i>y</i>	<i>z</i>	<i>a=b</i>	<i>c</i>
Li3a	<i>Li</i>	<i>3a</i>	0	0	0	2.82	14.10
	<i>Co</i>	<i>3b</i>	0	0	0.5		
	<i>O</i>	<i>6c</i>	0	0	0.2445		
Li3b	<i>Li</i>	<i>3b</i>	0	0	0.5	2.82	14.10
	<i>Co</i>	<i>3a</i>	0	0	0		
	<i>O</i>	<i>6c</i>	0	0	0.2445		

CONCLUSIONS

From the calculation of the total energy and electronic band structure of Li3a and Li3b, results show that the desired position of Li⁺ in the layered LiCoO₂ is the 3a Wyckoff positions (*x, y, z* = 0, 0, 0) as simulated by the Li3a structure. Band gap values of the Li3a structure is nearer to the experimental values than Li3b structure. Thus, Li⁺ in the 3a Wyckoff position presents a more stable structure for the hexagonal *R-3m* LiCoO₂ crystal structure.

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REFERENCES

1. Liu C, Neale Z G and Cao G 2016 Understanding electrochemical potentials of cathode materials in rechargeable batteries **19**
2. Tian N, Gao Y, Li Y, Wang Z, Song X and Chen L 2016 Lithium Ion Batteries Li₂C₂, a High-Capacity Cathode Material for Lithium Ion Batteries 644–8

3. Ozawa K 1994 Lithium-ion rechargeable batteries with LiCoO₂ and carbon electrodes : the LiCoO₂ / C system **69** 212–21
4. Jo M, Jeong S and Cho J 2010 Electrochemistry Communications High power LiCoO₂ cathode materials with ultra energy density for Li-ion cells *ELECOM* **12** 992–5
5. Xiong F, Yan H J, Chen Y, Xu B, Le J X and Ouyang C Y 2012 The Atomic and Electronic Structure Changes Upon Delithiation of LiCoO₂ : From First Principles Calculations **7** 9390–400
6. Shao-horn Y, Croguennec L, Delmas C, Nelson E C and Keefe M A O 2003 Atomic resolution of lithium ions in LiCoO₂ **2** 2–5
7. Clark S J, Segall M D, Pickard C J, Hasnip P J, Probert M I J, Refson K and Payne M C 2005 First principles methods using CASTEP *Zeitschrift für Krist.* **220** 567–70
8. Perdew J P, Burke K and Ernzerhof M 1996 Generalized Gradient Approximation Made Simple *Phys. Rev. Lett.* **77** 3865–8
9. Rappe A M, Rabe K M, Kaxiras E and Joannopoulos J D 1990 Optimized pseudopotentials *Phys. Rev. B* **41** 1227–30
10. Andriyevsky B, Doll K and Jacob T 2014 Electronic and transport properties of LiCoO₂ *Phys. Chem. Chem. Phys.* **16** 23412–20
11. Ghosh P, Mahanty S, Raja M W, Basu R N and Maiti H S 2007 Structure and optical absorption of combustion-synthesized nanocrystalline LiCoO₂ *J. Mater. Res.* **22** 1162–7
12. Kushida K and Kuriyama K 2002 Narrowing of the Co-3d band related to the order – disorder phase transition in LiCoO₂ **123** 349–52
13. van Elp J, Wieland J L, Eskes H, Kuiper P, Sawatzky G A, de Groot F M F and Turner T S 1991 Electronic structure of CoO, Li-doped CoO and LiCoO₂ *Phys. Rev. B* **44** 6090–103