

PAPER • OPEN ACCESS

Density Functional Theory Study of $\text{Li}_3\text{VO}_4\text{-}\delta$

To cite this article: Jianjian Shi and Zhiguo Wang 2019 *IOP Conf. Ser.: Earth Environ. Sci.* **300** 042001

View the [article online](#) for updates and enhancements.

Density Functional Theory Study of $\text{Li}_3\text{VO}_{4-\delta}$

Jianjian Shi and Zhiguo Wang*

School of Electronic Science and Engineering, University of Electronic Science and Technology of China, Chengdu, 610054, P.R. China

*Corresponding author e-mail: zgwang@uestc.edu.cn

Abstract. The large intrinsic band gap of Li_3VO_4 hinders its potential application as anode material for lithium ion batteries. Here, we perform first-principles calculations to investigate structural relaxation, formation energy, surface energy and electronic structure. The O vacancy in the Li_3VO_4 -(110) surface can enhance charge transfer and to improve the electron conductivity. This work indicates that $\text{Li}_3\text{VO}_{4-\delta}$ would be a potential anode material for batteries due to greater electron conductivity than the pristine Li_3VO_4 .

1. Introduction

Lithium ion batteries (LIBs) have been widely used in portable electronic devices with graphite as anode. However, the low specific capacity of graphite [1, 2] cannot satisfy the high energy density demands as power supplier for electronic vehicles and stationary grid storage. Li_3VO_4 (LVO)[3] can deliver a specific energy capacity of $\sim 400 \text{ mAh}\cdot\text{g}^{-1}$, with low voltage window between 0.2 V and 1V, which attracted much attention to be used as anode for LIBs.

However, during the first charge/discharge process, the poor electronic conductivity and coulombic efficiency hindered seriously the application of LVO as anode material for LIBs. Many efforts have been made to improve the electronic conductivity and coulombic efficiency of LVO anode through nano-structured LVO and carbon-coating. The nano-sized LVO shows high charging capacity of 422 mAh/g [4], However, both of these efforts can cause additional negative effects, such as large irreversible capacity loss or smaller volumetric energy density.

Recently, Yang [5] et al. reported that the amorphous and oxygen-deficient surface of LVO can enhance the charge kinetics, thus resulting in improvements in reversible capacity. These improvements has improved charge-transfer kinetics of $\text{Li}_3\text{VO}_{4-\delta}$ [5]. Moreover, the voltage gap in $\text{Li}_3\text{VO}_{4-\delta}$ ($\sim 0.39\text{V}$) is smaller than that of pristine LVO ($\sim 0.5\text{V}$). Fundamental understanding of electronic structure of LVO surface is crucial to improve the electrochemical performance of those electrode materials. The surface oxygen defects affect electrochemical properties of LVO is still not been studied by density functional theory. In this work, formation energy, surface energy and electronic structure of LVO surface were investigated based on the DFT.

2. Simulation methodology

It is performed using the SIESTA package in this work [6, 7]. A linear combination of numerical localized atomic orbital basis sets was used for the description of valence electrons [8]. The projector augmented wave (PAW) method [9] was used to describe electron-ion interactions. Generalized gradient approximation with the Perdew-Burke-Ernzerhof (PBE) function was used to describe the electron



exchange-correlation. The spin-polarization was considered for all the calculations. The valence electron wave functions were expanded using a DZP basis set (a double- ζ basis set plus polarization functional).

The unit cell of LVO was composed of 6 Li, 2 V and 8 O atoms. The atomic position and lattice vectors were relaxed with a $4 \times 4 \times 6$ Monkhorst-Pack [14] mesh sampling. The perfect LVO-(110) surface was modeled with symmetric slab which consisted of 60 Li, 20 V and 80 O atoms. A $2 \times 2 \times 1$ k-point mesh was used for the optimization LVO-(110) and the calculations of O vacancy formation on Li₃VO₄-(110) surface. A vacuum layer of 30 Å was used to avoid the interactions between adjacent mirror images caused by periodic boundary conditions. An energy cut-off was set to be 180 Ry. The geometric optimization was performed using a conjugate gradient method until the maximum force was less than 0.02 eV/Å.

3. Results and discussion

The crystalline structure of LVO is tetragonal structure with space group pnm21. The polyhedral configuration of unit cell for LVO is shown in Fig. 1(a).

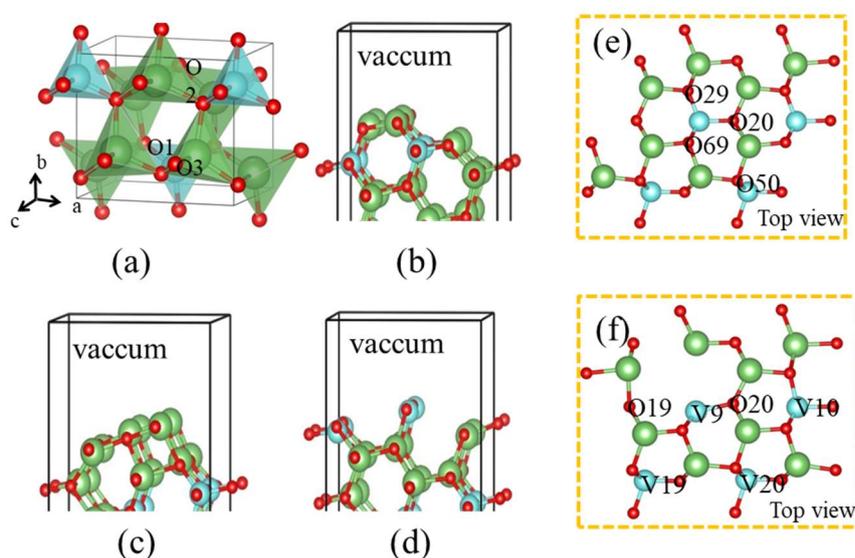


Figure 1. (a) Crystallographic structures of the bulk Li₃VO₄. The red, green and blue balls represent O, Li and V atoms, respectively. (b) Surface crystalline structure with Li-O (1)- terminated is self-complementary surfaces, (c) and (d) with Li-O (2)- and Li-V-O-terminated surfaces are complementary surfaces. (e) and (f) are the top view for the perfect LVO-(110) and the LVO-(110) surface with one O vacancy, respectively.

In order to compare the formation of O vacancy on the LVO (110) surface and in the bulk LVO, we firstly studied the surface stability of LVO (110) surface. There exist three types of terminations for LVO (110) surface, i.e. Li-O (1)-, Li-O (2)- and Li-V-O-terminations. The two adjacent surfaces are complementary surfaces. There are two pairs of complementary surfaces for LVO (110) surface are shown in Fig. 1(b), (c) and (d), Li-O (1)-terminated surface is self-complementary, Li-O (2)- and Li-V-O-terminated surfaces are complementary surface.

The surface energies for LVO (110) surface with different terminations are calculated based on DFT, which are 0.68, 2.86 and 3.12 J/m² for LVO (110) surface terminated with Li-O (1)-, Li-O (2)- and Li-V-O-terminations, respectively. (110) surfaces with Li-O (1)-termination has the lowest surface energies, so it is energetically stable surface for LVO. There are three types of O (O1, O2 and O3) in bulk LVO, as shown in Fig. 1(a). Four types of O vacancies (O20, O29, O50 and O69) for the LVO (110) surface were investigated. The formation energies of O vacancies in the bulk and the surface are in the range of 3.75~3.90 eV and 2.18~2.85 eV, respectively, which indicates O vacancy maybe easily formed on the

LVO (110) surface. The formation energy of O₂₉ vacancy is the smallest among the four types of oxygen vacancies. This result indicates that O-deficiency may appear in the surface of LVO. The relaxed atomistic structures of the perfect LVO (110) surface and the one with O₂₉ vacancy are shown in Fig. 1 (e) and (f), respectively.

The calculated band gaps of bulk LVO and surface LVO are 3.77 and 3.65 eV, which are in great agreement with the optical gap energy 3.7-3.9 eV [8]. The Fermi level was set to be zero. The DOS of the perfect LVO (110) and LVO (110) with one O vacancy were shown in Fig. 2. The Fermi level of LVO with one O vacancy was substantially increased to just below the conduction band minimum and there are defect levels above Fermi level compared to the perfect LVO (110). This suggests that the existence of O vacancy in the LVO-(110) surface facilitates the charge transfer, which is in good agreement with the experimental prediction [4], resulting in great improvements in the electrochemical properties.

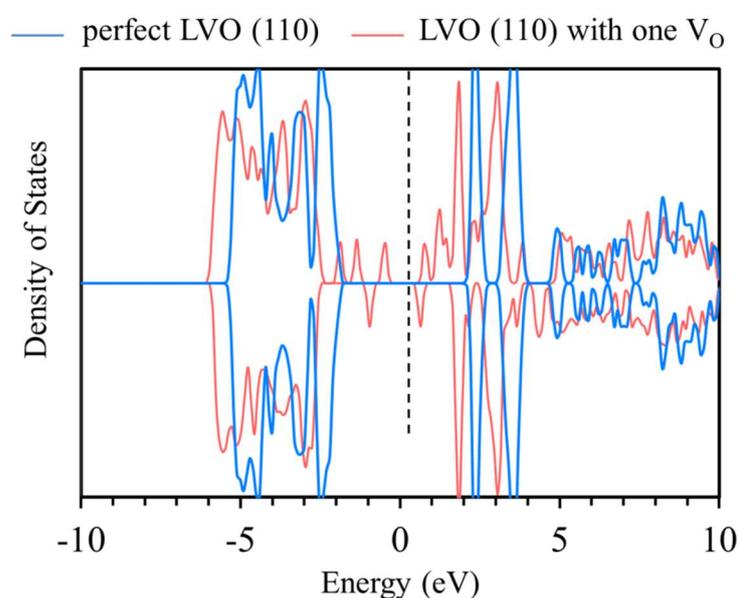


Figure 2. Blue and red lines represent the total density of states for the perfect LVO (110) the LVO-(110) with one O vacancy, respectively.

4. Conclusion

In summary, first-principles calculations based on DFT have been carried out to investigate the structural relaxation, formation energy, electronic structure of the bulk Li_3VO_4 . The O vacancy in the surface can improve effectively the electronic conductivity of the LVO. It will facilitate the charge transfer of Li_3VO_4 as anode material for LIBs and improve electrochemical properties of electrode materials.

References

- [1] P. Ganesh, P.R.C. Kent, D.-e. Jiang, Solid-Electrolyte Interphase Formation and Electrolyte Reduction at Li-Ion Battery Graphite Anodes: Insights from First-Principles Molecular Dynamics, *The Journal of Physical Chemistry C*, 116 (2012) 24476-24481.
- [2] P. Novak, F. Joho, R. Imhof, J.C. Panitz, O. Haas, In situ investigation of the interaction between graphite and electrolyte solutions, *Journal of Power Sources*, 81 (1999) 212-216.
- [3] K. Wang, C. Zhang, H. Fu, C. Liu, Z. Li, W. Ma, X. Lu, G. Cao, Enhanced Electrochemical Properties of Li_3VO_4 with Controlled Oxygen Vacancies as Li-Ion Battery Anode, *Chemistry – A European Journal*, 23 (2017) 5368-5374.
- [4] L.-L. Zhou, S.-Y. Shen, X. Peng, L.-N. Wu, Q. Wang, C.-H. Shen, T.-T. Tu, L. Huang, J.-T. Li, S.-G. Sun, New insights into the structure changes and interface properties of Li_3VO_4 anode for lithium ion batteries during the initial cycle by in-situ techniques, *ACS applied materials*

- & interfaces, (2016).
- [5] L. Chen, X.L. Jiang, N.N. Wang, J. Yue, Y.T. Qian, J. Yang, Surface-Amorphous and Oxygen-Deficient Li_3VO_4 -delta as a Promising Anode Material for Lithium-Ion Batteries, *Adv Sci*, 2 (2015).
 - [6] J.P. Perdew, K. Burke, M. Ernzerhof, Generalized gradient approximation made simple, *Phys Rev Lett*, 77 (1996) 3865-3868.
 - [7] J.M. Soler, E. Artacho, J.D. Gale, A. Garcia, J. Junquera, P. Ordejon, D. Sanchez-Portal, The SIESTA method for ab initio order-N materials simulation, *J Phys-Condens Mat*, 14 (2002) 2745-2779.
 - [8] N. Troullier, J.L. Martins, EFFICIENT PSEUDOPOTENTIALS FOR PLANE-WAVE CALCULATIONS, *Physical Review B*, 43 (1991) 1993-2006.
 - [9] G. Kresse, D. Joubert, From ultrasoft pseudopotentials to the projector augmented-wave method, *Phys. Rev. B*, 59 (1999) 1758-1775.