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Evaluating Electrical Properties, Band Gaps and Rate Capability of Li_2MSiO_4 (M= Mn, Fe, Co, Ni) Cathode Materials Using DOS Diagrams

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ABSTRACT

In this study, theoretical investigations of Li_2MSiO_4 family cathode materials, including Li_2MnSiO_4, Li_2FeSiO_4, Li_2CoSiO_4, and Li_2NiSiO_4 are performed using density functional theory (DFT), by GGA and GGA+U methods. The materials properties including electrical conductivity and rate capability were investigated. To evaluate electrical conductivity, we use here a noble approach in DFT established in our previous work, which is related to intrinsic/extrinsic band gap concepts in solid state physics. Also, using lithiated-delithiated junction, aligning Fermi levels, and the difference between conduction bands value is the basis of the comparison of rate-capability, which is also a noble approach. To perform a quantitative investigation of electrical rate-capability, Fermi levels of obtained DOS diagrams of lithiated and delithiated structures were aligned. The difference between maximum of valance band (MVB) of lithiated and delithiated structures was considered as the criteria of rate-capability. The obtained values for the considered materials were fairly close. It was concluded that electron conductivity and rate-capability of this family of Li-ion cathode material is in the same range and do not strictly relate to the transition metal.

1. INTRODUCTION

As potential cathode materials, the electrochemical behavior of poly-anion compounds olivine-structured formulated as $LiMPO_4$ and Li_2MSiO_4 (M= Mn, Co, Fe, Ni) have been attracted and raised much interests [1-5]. Zhou et al. [6] have been reported a study including a comparison between lithium intercalation potential in mentioned transition metal compounds.

Compounds with olivine structure have advantages among other cathode materials including structural stability, and wide voltage range. Among the phosphate compounds, $LiFePO_4$ has the greatest amount of attention according to a number of features such as non-toxicity, low cost, chemical and thermal stability [7,8]. The main disadvantage of lithium iron phosphates, $LiFePO_4$, is their low rate capability and electrochemical performance due to poor electronic conductivity and low lithium-ion diffusion [5]. To overcome this drawback, many material processing techniques, including coatings of phosphate nanoparticles with carbon and doping with metals have been proposed [8].

The other group of poly-anion compounds, silicates, is potentially interesting cathode materials. Li_2FeSiO_4 [9,10], Li_2MnSiO_4 [11,12] and Li_2CoSiO_4 [13,14] have been experimentally evaluated in this family of cathodes. However, several limitations have to be passed before such materials become commercially usable. The most important challenges are rate-capabilities and electrical conductivities [15].

Parameters that affect rate-capability of cathodes could be divided into two main issues including electron conductivity and ion conductivity.

Kalantarian et al. [5] have suggested that the rate-capability of a cathode should be considered as a junction of lithiated-delithiated structures instead of considering the structures separately. In the next work Kalantarian et al. [16] also addressed a new quantitative approach to compare rate capability of cathode materials in one family, evaluating layered oxide cathode materials as an important pioneer case study. Moreover, they proposed new definitions of band-gap to evaluate electronic conductivity in DFT framework [16].

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Regarding electron conductivity, a new insight of density of states, DOS, diagrams for assessment of band gaps, so conductivity, has been proposed [16]. Here, we are using our noble approaches, which have proposed in the DFT studies [5,16], to evaluate electrical properties of the $LiMSiO_4$ battery cathode materials family. The proposed approaches were opening new evaluation land space for evaluation of band-gaps, calling them extrinsic-like and intrinsic-like band gap.

According to ref. [5], calculated electronic bands by DFT in DOS (or band structure) diagrams could be divided into two different types: electronic bands created by *d* or *f* orbitals, and the bands created by the other orbitals. It is because the estimated DOS by DFT for *d* or *f* orbitals is not reliable [18] in contrast with the other orbitals [5]. Accordingly, two different types of band gap (BG) have been considered. The difference between lowest energy above Fermi level and the highest energy below it in a DOS diagram is defined as "extrinsic-like band gap" (ELBG). Another kind of band gap can be deliberated by ignoring the bands created by *d* or *f* orbitals (may be called donor/acceptor bands [5]) and considering the energy gap between the highest energy below Fermi level and the lowest energy above it. It has been called as "intrinsic-like band gap" (ILBG).

In this study, we used DFT methods to consider the electrical properties of the $LiMSiO_4$ cathode materials and we compare them as a term of understanding the properties and comparing the advantages and disadvantages of each one.

2. METHODOLOGY

Evaluated structure is given from refs. [2,3,18]. The space group of the considered structure is $Pmn2_1$. Figure 1 shows the structure in its lithiated and delithiated state. The configuration of Li atoms shown in Figure 1b is the most stable configuration [2,4,19].

All the calculations in this work were performed using full-potential linear augmented plane wave (FP-LAPW) method within the framework of density functional theory (DFT) [20], as implemented in the WIEN2K code.[20] For the assessment of the properties, including density of states (DOS), the calculations were carried out using Perdew–Burke–Ernzerh generalized gradient approximation (PBE-GGA) [4] and generalized gradient and local density approximations plus an on-site Coulomb self-interaction correction potential ($GGA+U^{SIC}$). Inside the non-overlapping spheres of muffin tin radius (RMT) around each atom, the linear combination of radial solution of the Schrödinger equation times the spherical harmonics are used and the plane-wave basis set is used in the interstitial region. RMT values 2.00, 1.90, 1.86, 1.75 and 1.78 a.u. were used for Mn, Fe, Co, Ni, and Li, respectively, and 1.52 a.u. for Si and O atoms. To expand the wave functions in the interstitial region a plane wave cut-off value of K_{max}. RMT =7.0 was used. The Fourier-expanded charge density was truncated at $G_{max}=12\ (Ryd)^{1/2}$. The maximum value of the angular momentum (l_{max}) was set equal to 10 for the wave function expansion inside the atomic spheres. The convergence of the self-consistent iterations was performed within 0.0001 Ry.

All the calculations were carried out using spin polarization of the transition metals orbitals.

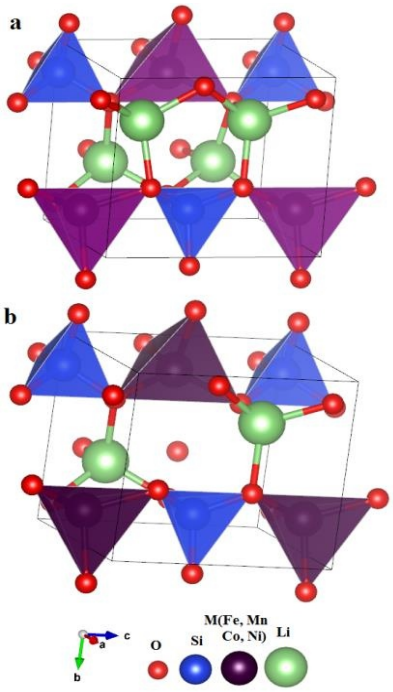

Figure 1. Illustration of the evaluated structure ($Pmn2_1$ space group) in its lithiated (a) and delithiated (b) states

3. RESULTS AND DISCUSSION

We have defined two kinds of band-gap in our recent work [16], named intrinsic-like and extrinsic-like. The intrinsic-like band gap (ILBG) is shown in Figures 2 and 3 as the distance between blue and yellow areas. Considering the bands created by *3d* orbitals would be the donor/acceptor bands in DOS[5].

3.1. Conductivity

As far as extrinsic-like band gap (ELBG) would be considered as a criterion of conductivity, only GGA+U calculations are reportable, due to the well-known errors caused by *3d* orbitals in GGA calculations. Obtained ELBGs by GGA+U and GGA are shown in Table 1. Considering ELBG of lithiated structures, Li_2FeSiO_4-Li_2NiSiO_4, Li_2CoSiO_4, and Li_2MnSiO_4 exhibited the best to the worst electron conductivity, respectively (regarding both GGA and GGA+U methods, Table 1). According to the table (ELBG

values), delithiation generally results in better electron conductivity. The best to the worst conductivity for delithiated structures based on GGA+U calculation belongs to: $LiNiSiO_4$, $LiMnSiO_4$, $LiCoSiO_4$, and $LiFeSiO_4$, respectively. As conclusions, ELBG approach predicts Li_2FeSiO_4-Li_2NiSiO_4 has most electron conductivity in lithiated structure; whereas, in delithiated condition, Li_2NiSiO_4 is the best. ELBG approach predicts Li_2MnSiO_4 has the least electron conductivity in lithiated structure; whereas, in delithiated condition, Li_2FeSiO_4 is the worst.

TABLE 1. Extrinsic-like band gap (ELBG) of the lithiated/delithiated materials calculated by GGA and GGA+U, per eV

method	material	lith.	delith.
GGA	Li_2MnSiO_4	1.6	-
	Li_2FeSiO_4	0.2	0.6
	Li_2CoSiO_4	0.3	0.1
	Li_2NiSiO_4	0.2	-
GGA+U	Li_2MnSiO_4	4	1
	Li_2FeSiO_4	3.1	2.4
	Li_2CoSiO_4	3.5	1.9
	Li_2NiSiO_4	3.1	0.9

The obtained intrinsic-like band gaps (ILBGs) by GGA and GGA+U methods are shown in Table 2.

TABLE 2. Calculated intrinsic-like band gap (ILBG) per eV of the lithiated/delithiated materials by GGA and GGA+U, per eV

method	material	lith.	delith.
GGA	Li_2MnSiO_4	6.0	4.1
	Li_2FeSiO_4	5.8	4.1
	Li_2CoSiO_4	5.7	4.5
	Li_2NiSiO_4	5.7	5.0
GGA+U	Li_2MnSiO_4	4.0	5.5
	Li_2FeSiO_4	5.0	5.2
	Li_2CoSiO_4	4.8	5.2
	Li_2NiSiO_4	5.1	5.8

It could be noticed that in ILBG approach, in contrast with ELBG, GGA method is more reliable than GGA+U one [16]. As far as considering ILBG as the criterion of conductivity, the best (worst) predicted conductivities of delithiated materials belong to Li_2FeSiO_4 (Li_2NiSiO_4) for both calculated methods. This ranking is opposite to the ranking obtained by ELBG (for this kind of material). According to the table, for lithiated structures, the best (worst) obtained conductivity belongs to Li_2CoSiO_4-Li_2NiSiO_4 (Li_2MnSiO_4) for GGA -the more reliable- calculation method. Also, ILBG values are not altering so much by altering the transition metal. Delithiation causes better conductivity in both ELBG and ILBG approaches. It is in contrast with oxide cathode materials [16].

3.2. Rat Capability

It is shown that to consider (dis)charge rate resulted from electron conductivity, the lithiated-delithiated junction should be considered rather than conductivity of lithiated and delithiated structures in separate. In the previous work [5], the comparison of the materials in rate-capability had been qualitative between different kinds of materials which are based on different structures. Like our previous work, here, we use a quantitative approach comparing rate-capability of materials with the same structures (in one family) in the same frame-work calculation.

These materials are semiconductors in lithiated and delithiated states [5]. Considering that, a junction will be made in lithiated and delithiated structures in (dis)charge process [5,20-23]. In their equilibrium state, the Fermi level is constant for whole parts of the material, which is well-known for junctions. This fact is considered for showing lithiated-delithiated DOS diagrams in Figures 2 and 3. In the figures, the Fermi level of the lithiated and delithiated structures for each cathode material was aligned. In Figure 2, considering intrinsic-like bands (ILBs), the difference between maximum of valance band (MVB) of delithiated structure with MVB in lithiated one, hereinafter called Δ(V.B.), is written for each diagram. For Figures 2 and 3, considering intrinsic-like bands, the difference between minimum of conduction band (MCB) in delithiated structure with MCB in lithiated one, hereinafter called Δ(C.B.), is written for each diagram.

According to ref [17], Δ(V.B.) and Δ(C.B.) could be demonstrative as rate-capability indicator.

These materials acting like N-type/P-type semiconductors in lithiated/delithiated state (Fermi level is closer to intrinsic conduction/valance band, in GGA). Therefore, the majority of charge carriers are holes (located in valance band) not electrons (located in conduction band).

Location of Fermi energy in DOS (for ILBG) obtained by GGA is more reliable than that of GGA+U [5]. It is because of effecting of U^{SIC} potential on Fermi energy. Also, for this kind of material Δ(C.B.) is more reliable than Δ(V.B.), because its value is less.

Considering Δ(C.B.) of the GGA method, sort of the materials is Li_2MnSiO_4-Li_2NiSiO_4, Li_2CoSiO_4 and Li_2FeSiO_4, (the best to the worst in rate-capability) respectively. As a report, considering Δ(V.B.) of GGA, Li_2NiSiO_4 and Li_2FeSiO_4 have the best and the worst rate-capability, as well as Δ(C.B.) of GGA.

4. CONCLUSION

In this study, noble approaches were used to evaluate conductivity in DFT calculations, considering intrinsic-like and extrinsic-like band gap (ILBG and ELBG, respectively) using DOS diagrams. As it is well known, calculated ELBGs by GGA method is not realistic. Nevertheless, DOS calculated by the GGA method is useful to determine the type of semiconductor by evaluating relative location of the Fermi level in ILBG. Calculated ILBG values (by both GGA and GGA+U methods) of the considered materials did not change remarkably by substitution of the transition-metals with each other. Delithiation causes increasing (decreasing) ILBG (ELBG) values. Electrical rate-capability was investigated quantitatively by aligning Fermi levels DOS diagrams of lithiated and delithiated structures and comparing the energy difference of VBMs or CBMs of each pair.

Although we sorted the considered materials based on differences between the obtained values, however, fairly the values are close. As a conclusion, we conclude that electron conductivity and rate-capability of this family of Li-ion cathode materials are in the same range.

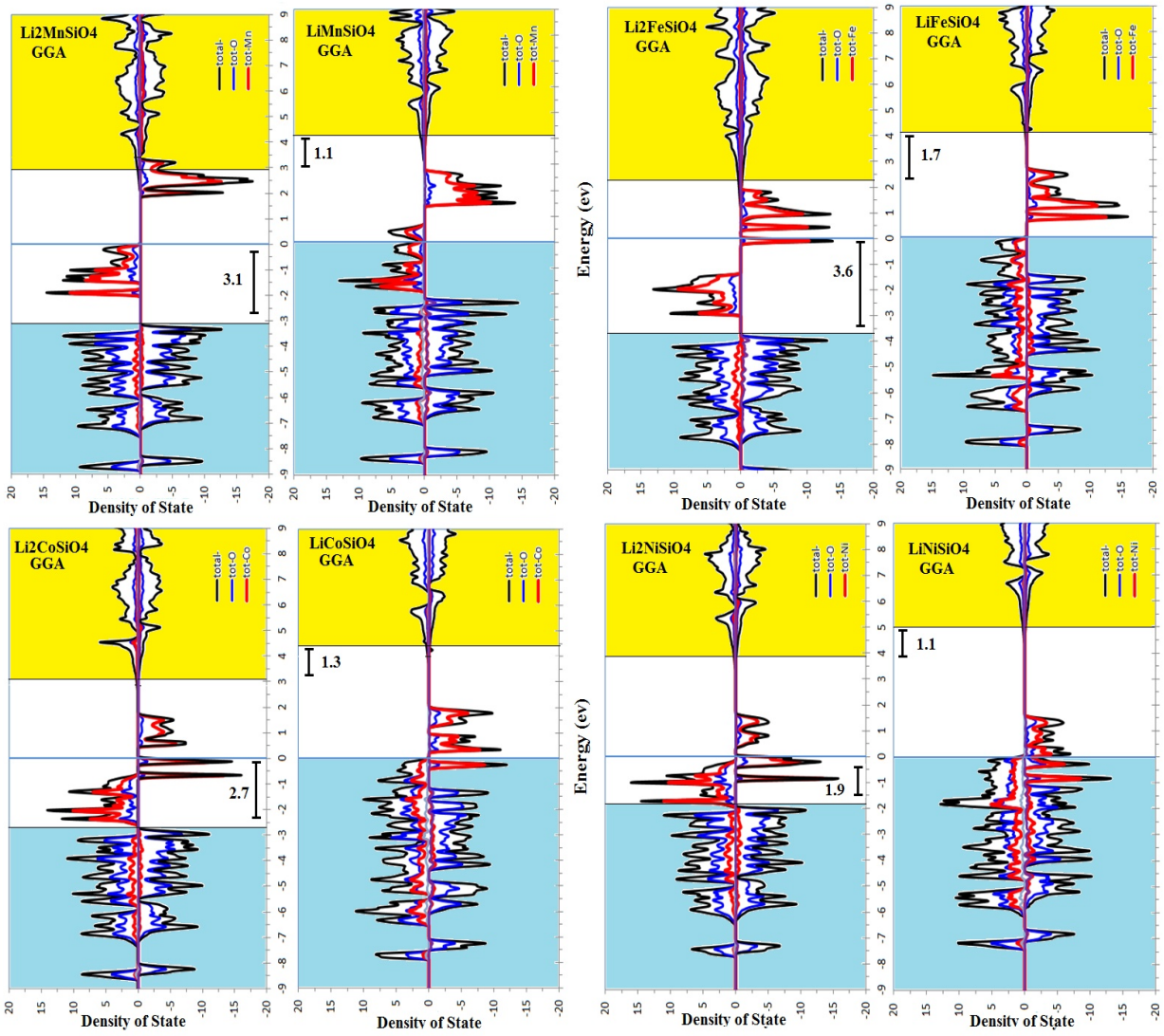

Figure 2. Density of States (DOS) for the cathode materials before and after lithium excretion, calculated by GGA. The levels produced by *3d* orbitals lie under/above Fermi level are shown in red/green color. Fermi level set as zero and aligned for each lithiated-delithiated pair. Δ(V.B.) and Δ(C.B.) values are written in bottom and top of each pair, respectively.

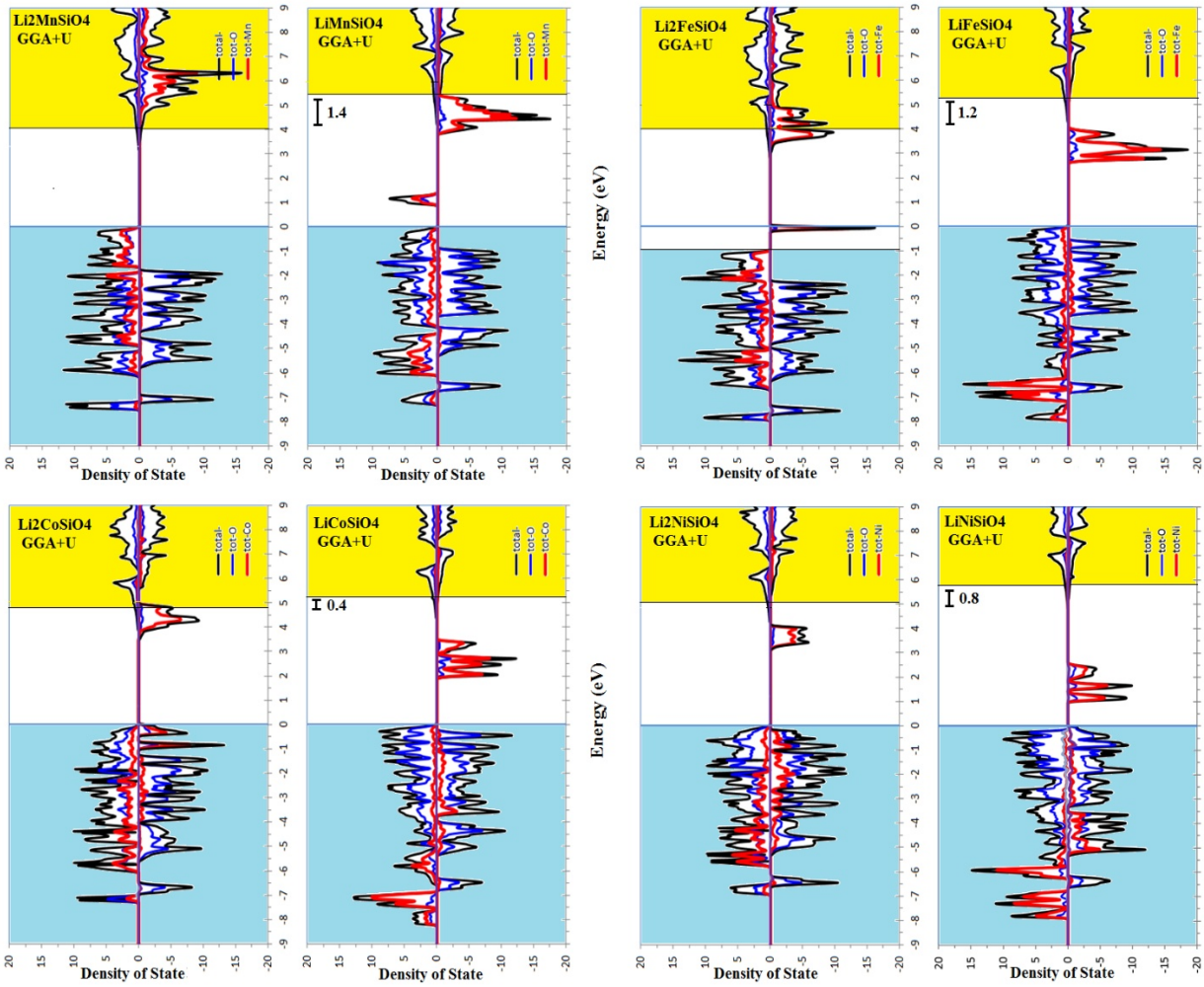

Figure 3. Obtained DOS for cathode materials before and after lithium excretion, calculated by GGA+U. Fermi level set as zero and aligned for each lithiated-delithiated pair. Δ(C.B.) values are written in top of each pair.

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REFERENCES

1. Kalantarian, M. M., Asgari, S., Capsoni, D., Mustarelli, P., "An ab initio investigation of $Li_2M_{0.5}N_{0.5}SiO_4$ (M, N= Mn, Fe, Co Ni) as Li-ion battery cathode materials", ***Physical Chemistry Chemical Physics***, Vol. 15, No. 21, (2013), 8035-8041.
2. Kalantarian, M. M., Asgari, S., "Theoretical Assessment of the First Cycle Transition, Structural Stability and Electrochemical Properties of Li_2FeSiO_4 as a Cathode Material for Li-ion Battery", ***Advanced Ceramics Progress***, Vol. 3, No. 4, (2017), 25-33.
3. Kalantarian, M. M., Oghbaei, M., Asgari, S., Karimi, L., Ferrari, S., Capsoni, D., Bini, M., Mustarelli, P., "Electrochemical Characterization of Low-Cost Lithium-Iron Orthosilicate Samples as Cathode Materials of Lithium-Ion Battery", ***Advanced Ceramics Progress***, Vol. 3, No. 3, (2017), 19-25.
4. Kalantarian, M. M., Asgari, S., Mustarelli ,P., "Theoretical investigation of Li_2MnSiO_4 as a cathode material for Li-ion batteries: a DFT study", ***Journal of Materials Chemistry A***, Vol. 1, No. 8, (2013), 2847-2855.
5. Kalantarian, M. M., Asgari, S., Mustarelli, P., "A theoretical approach to evaluate the rate capability of Li-ion battery cathode materials", ***Journal of Materials Chemistry A***, Vol. 2, No. 1, (2014), 107-115.
6. Zhou, F., Cococcioni, M., Kang, K., Ceder, G., "The Li intercalation potential of $LiMPO_4$ and $LiMSiO_4$ olivines with M= Fe, Mn ,Co, Ni", ***Electrochemistry Communications***, Vol. 6, No. 11, (2004), 1144-1148.
7. Guo, H.-J. Xiang, K.X., Xuan, C.A.O., Li, X.H., Wang, Z.X., Li, L.M., "Preparation and characteristics of Li2FeSiO4/C

composite for cathode of lithium ion batteries", ***Transactions of Nonferrous Metals Society of China***, Vol. 19 , No. 1, (2009), 166-169.

8. Kazazi, M ,.Illbeigi, M., Fazlali, A. & Mohammadi, A., "Preparation, characterization and stability of Li-ion conducting $Li_{1.5}Al_{0.5}Ge_{1.5}(PO_4)_3$ glass-ceramic with NASICON-type structure", ***Advanced Ceramics Progress***, Vol. 2, No. 1, (2016), 38-43.
9. Dahbi, M., Urbonaite, S., Gustafsson, T., "Combustion synthesis and electrochemical performance of Li_2FeSiO_4/C cathode material for lithium-ion batteries", ***Journal of Power Sources***, Vol. 205, (2012), 456-462.
10. Zhang, S., Deng, C., Fu, B., Yang, S., Ma, L., "Effects of Cr doping on the electrochemical properties of Li_2FeSiO_4 cathode material for lithium-ion batteries", ***Electrochimica Acta***, Vol. 55, No. 28, (2010), 8482-8489.
11. Dominko, R., Bele, M., Kokalj, A., Gaberscek, M., Jamnik, J., "Li_2MnSiO_4 as a potential Li-battery cathode material", ***Journal of Power Sources***, Vol. 174, No. 2, (2007), 457-461.
12. Gummow, R., Sharma, N., Peterson, V., He, Y., "Synthesis, structure, and electrochemical performance of magnesium-substituted lithium manganese orthosilicate cathode materials for lithium-ion batteries", ***Journal of Power Sources***, Vol. 197, (2012), 231-237.
13. Gong, Z., Li, Y., Yang, Y., "Synthesis and electrochemical performance of Li_2CoSiO_4 as cathode material for lithium ion batteries", ***Journal of Power Sources***, Vol. 174, No. 2, (2007), 524-527.
14. Wu, S. Q., Zhang, J. H., Zhu, Z. Z., Yang, Y., "Structural and electronic properties of the Li-ion battery cathode material $LixCoSiO_4$", ***Current Applied Physics***, Vol. 7, No. 6, (2007), 611-616.
15. Kalantarian, M. M., Oghbaei, M., Asgari, S., Ferrari, S., Capsoni, D., Mustarelli, P., "Understanding non-ideal voltage behaviour of cathodes for lithium-ion batteries", ***Journal of Materials Chemistry A***, Vol. 2, No. 45, (2014), 19451-19460.
16. Momeni, M., Mashhour, H. Y., Kalantarian, M. M., "New approaches to consider electrical properties, band gaps and rate capability of same-structured cathode materials using density of states diagrams: Layered oxides as a case study", ***Journal of Alloys and Compounds***, Vol. 787, (2019), 738-743.
17. Perdew, J. P., Yang, W., Burke, K., Yang, Z., Gross, E.K., Scheffler, M., Scuseria, G.E., Henderson, T.M., Zhang, I.Y., Ruzsinszky, A., Peng, H., "Understanding band gaps of solids in generalized Kohn–Sham theory", ***Proceedings of the National Academy of Sciences***, Vol. 114, No. 11, (2017), 2801-2806.
18. Nytén, A., Abouimrane, A., Armand, M., Gustafsson, T., Thomas, J. O., "Electrochemical performance of Li_2FeSiO_4 as a new Li-battery cathode material", ***Electrochemistry Communications***, Vol. 7, No. 2, (2005), 156-160.
19. Nytén, A., Kamali, S., Häggström, L., Gustafsson, T., Thomas, J. O., "The lithium extraction/insertion mechanism in Li_2FeSiO_4 ,"***Journal of Materials Chemistry***, Vol. 16, No. 23, (2006), 2266-2272.
20. Perdew, J. P., "k. Burke, m. ernzerhof", ***Physical Review Letters***, Vol. 77, (1996), 3865.
21. Delmas, C., Maccario, M., Croguennec, L., Le Cras, F., Weill, F., "Lithium deintercalation in $LiFePO_4$ nanoparticles via a domino-cascademodel" in Materials For Sustainable Energy: A Collection of Peer-Reviewed Research and Review Articles from Nature Publishing Group, (2011), 180-186.
22. Wang, J., Chen-Wiegart, Y.C. K., Wang, J., "In operando tracking phase transformation evolution of lithium iron phosphate with hard X-ray microscopy", ***Nature communications***, Vol. 5, (2014), 4570.
23. Zhu, H., Wu, X., Zan, L., Zhang, Y., "Superior electrochemical capability of Li_2FeSiO_4/C/G composite as cathode material for Li-ion batteries", ***Electrochimica Acta***, Vol. 117, (2014), 34-40.