Electronic and Atomic Structures of LiMPO_4 ($M = \text{Fe}, \text{Fe}_{1/4}\text{Mn}_{1/4}\text{Co}_{1/4}\text{Ni}_{1/4}$): A DFT Study

Bo Jin*, Ren Qin Zhang, and Qing Jiang

Key Laboratory of Automobile Materials, Ministry of Education, and College of Materials Science and Engineering,
Jilin University, Changchun 130025, China

Electronic and atomic structures of $\text{LiFe}_{1/4}\text{Mn}_{1/4}\text{Co}_{1/4}\text{Ni}_{1/4}\text{PO}_4$ and LiFePO_4 were investigated by using the first-principles density functional theory. Our calculations demonstrate that doping Mn, Co and Ni atoms at Fe sites of LiFePO_4 enhances the electron localization at Fe sites, which leads to the metallic characteristics of $\text{LiFe}_{1/4}\text{Mn}_{1/4}\text{Co}_{1/4}\text{Ni}_{1/4}\text{PO}_4$. Thus, the electronic conductivity of $\text{LiFe}_{1/4}\text{Mn}_{1/4}\text{Co}_{1/4}\text{Ni}_{1/4}\text{PO}_4$ may be improved. The doped material is expected to be promising cathode material for rechargeable lithium-ion batteries.

Keywords: Cathode Materials, Structural Prediction, Band Gap, Lithium-Ion Batteries.

1. INTRODUCTION

Rechargeable lithium-ion batteries (LIBs) have been used widely in mobile phones, laptop computers, digital cameras, electrical vehicles and hybrid electrical vehicles.^{1–4} In rechargeable LIBs, the cathode material is a key component mainly relating to the performance of the batteries. Recently, lithium transition metal phosphates with ordered olivine-type structures, LiMPO_4 (where $M = \text{Fe}, \text{Mn}, \text{Ni}, \text{and Co}$), and lithium iron silicate ($\text{Li}_2\text{FeSiO}_4$) have attracted great attention as lithium insertion cathode materials for the next generation of rechargeable LIBs.^{5–11} The potential of the M^{3+}/M^{2+} redox couple versus Li/Li^+ of LiMPO_4 is as follows; 3.5 V for LiFePO_4 , 4.1 V for LiMnPO_4 , 5.2–5.4 V for LiNiPO_4 , and 4.8 V for LiCoPO_4 . Among them, LiFePO_4 is the most attractive because of its high stability, low cost and high compatibility with environment.^{12, 13} However, it is difficult to attain the full capacity because the electronic conductivity of LiFePO_4 ($\sim 10^{-9} \text{ S cm}^{-1}$) is very low, which leads to initial capacity loss and poor rate capability. In addition, the diffusion of Li^+ ion across the $\text{LiFePO}_4/\text{FePO}_4$ boundary is slow due to the intrinsic character of LiFePO_4 .⁵

Many researchers have suggested solutions to this problem, viz. (1) mixing carbon with the particles,¹⁴ (2) synthesis of particles with well-defined morphology¹⁵ and (3) metallic doping to enhance the electrochemical properties. Yamada et al.¹⁶ reported that the Mn-doped $\text{LiMn}_{0.6}\text{Fe}_{0.4}\text{PO}_4$ can deliver a discharge capacity of

greater than 160 mAh g^{-1} , and exhibits two pairs of voltage plateaus at 4.1 V ($\text{Mn}^{3+}/\text{Mn}^{2+}$) and 3.5 V ($\text{Fe}^{3+}/\text{Fe}^{2+}$). This is obviously different from the LiFePO_4 , in which the whole $\text{Fe}^{3+}/\text{Fe}^{2+}$ reaction proceeds in a two-phase way ($\text{LiFePO}_4\text{-FePO}_4$) with a voltage plateau at 3.4 V.⁵ Wang et al.¹⁷ reported $\text{LiFe}_{1-x}\text{Co}_x\text{PO}_4$ solid solutions keep a rather high capacity during 20 cycles, retaining 88.4% of the original capacity for $\text{LiFe}_{0.8}\text{Co}_{0.2}\text{PO}_4$, 86.3% for $\text{LiFe}_{0.5}\text{Co}_{0.5}\text{PO}_4$, and 88.1% for $\text{LiFe}_{0.2}\text{Co}_{0.8}\text{PO}_4$. Chen et al.¹⁸ synthesized successfully the ternary solid solution $\text{LiFe}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{PO}_4$ by the hydrothermal reaction with the lattice parameters of $a = 10.337 \text{ \AA}$, $b = 6.008 \text{ \AA}$, $c = 4.717 \text{ \AA}$, and volume = $292.95 \text{ \AA}^3$. A quaternary solid solution $\text{LiFe}_{1/4}\text{Mn}_{1/4}\text{Co}_{1/4}\text{Ni}_{1/4}\text{PO}_4$ with lattice parameters smaller than LiFePO_4 and larger than LiCoPO_4 has further been prepared,¹⁹ where there are three redox couples of $\text{Fe}^{3+}/\text{Fe}^{2+}$, $\text{Mn}^{3+}/\text{Mn}^{2+}$ and $\text{Co}^{3+}/\text{Co}^{2+}$ at ~ 3.6 , 4.2 and 4.7 V.²⁰ Also, Mn and Fe in the solid solution display high electrochemical activity in a voltage range of 3.0–5.1 V.¹⁹

The above studies show that the ionic substitution with Mn, Co and Ni at Fe sites of LiFePO_4 improves electrochemical performance. However, the detailed electronic and atomic structures of $\text{LiFe}_{1/4}\text{Mn}_{1/4}\text{Co}_{1/4}\text{Ni}_{1/4}\text{PO}_4$ still open, which is useful to consider physical background of the compound and find ways for further improvement of the electrochemical performance.

In this study, the structural performance of $\text{LiFe}_{1/4}\text{Mn}_{1/4}\text{Co}_{1/4}\text{Ni}_{1/4}\text{PO}_4$ including the lattice parameters and the electronic densities of states was quantitatively analyzed using the first-principles density functional

* Author to whom correspondence should be addressed.

theory (DFT) compared to LiFePO_4 . This is because DFT is a useful tool to realize the above goal.^{21–29}

2. COMPUTATIONAL METHOD

All the calculations in this work were carried out using the DMol3 package based on the first-principles DFT.^{30,31} We used the generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functionals and Double Numerical plus d-functions (DND) atomic orbitals as basis set.³² In the meantime, we also used the local density approximation (LDA) with the Perdew-Wang (PWC) exchange-correlation functionals.³³ The first-principles DFT semicore pseudopotentials (DSPP) treatment was implemented for relativistic effects, which replaces core electrons by a single effective potential.³⁴ Li 2s, Fe 3d and 4s, Mn 3d and 4s, Co 3d and 4s, Ni 3d and 4s, P 3s and 3p, and O 2s and 2p were regarded as the valence electrons, and all the others were regarded as the core electrons.

To study the doping effect, the calculations of the $1 \times 2 \times 1$ expanded supercell (56 atoms) for $\text{LiFe}_{1/4}\text{Mn}_{1/4}\text{Co}_{1/4}\text{Ni}_{1/4}\text{PO}_4$ and LiFePO_4 were performed, while the latter calculation was made for comparison purpose. The Brillouin zone of the supercell was sampled by $4 \times 4 \times 4$ k -points within the Monkhorst-Pack scheme.³⁵ Full structural optimizations were obtained with symmetry constraints using a convergence tolerance of energy of 2.0×10^{-5} hartree (1 hartree = 27.2114 eV), a maximum force is 0.004 hartree/Å and a maximum displacement of 0.005 Å. The orbital cutoff was set to be global, and smearing was 0.005 Ha.

In order to demonstrate the validity of our computational method, structural optimizations of LiFePO_4 were performed based on the bulk crystal structure observed experimentally.³⁶ The structural optimizations of $\text{LiFe}_{1/4}\text{Mn}_{1/4}\text{Co}_{1/4}\text{Ni}_{1/4}\text{PO}_4$, $\text{Fe}_{1/4}\text{Mn}_{1/4}\text{Co}_{1/4}\text{Ni}_{1/4}\text{PO}_4$ and FePO_4 are based on the optimized LiFePO_4 . The olivine-type crystal structures of $\text{LiFe}_{1/4}\text{Mn}_{1/4}\text{Co}_{1/4}\text{Ni}_{1/4}\text{PO}_4$ and LiFePO_4 in the $1 \times 2 \times 1$ expanded supercell (56 atoms) are orthorhombic (space group $Pnma$), and shown in Figure 1. As shown in Figure 1(a), one unit cell of LiFePO_4 contains four groups of three cation-centered polyhedrons; a PO_4 tetrahedron, a LiO_6 octahedron and a FeO_6 octahedron. As shown in Figure 1(b), one unit cell of $\text{LiFe}_{1/4}\text{Mn}_{1/4}\text{Co}_{1/4}\text{Ni}_{1/4}\text{PO}_4$ contains four groups of three cation-centered polyhedrons; the first group consists of a PO_4 , a LiO_6 and a FeO_6 , 2nd to 4th have the same two formers, while the third are MnO_6 , CoO_6 and NiO_6 , respectively. The calculated lattice parameters and atomic coordinates for LiFePO_4 and FePO_4 are listed in Table I, and compared with experimental values of LiFePO_4 .³⁶ As seen in Table I, in the GGA calculations, the lattice parameters ' a ' and ' b ' of LiFePO_4 decrease by 2.7%

Fig. 1. The crystalline structures of (a) LiFePO_4 and (b) $\text{LiFe}_{1/4}\text{Mn}_{1/4}\text{Co}_{1/4}\text{Ni}_{1/4}\text{PO}_4$.

and 2.9% compared with the experimental values, respectively, and ' c ' increases by 0.4% and the calculated volume decreases by 5.1%. We have also used LDA calculations, the obtained lattice parameters ' a ', ' b ' and ' c ' of LiFePO_4 decrease by 6.3%, 6.9% and 1.8%, respectively, and the calculated volume decreases by 14.4%. Thus, GGA has better calculation accuracy and thus is used in this work. Note that the lattice parameters of FePO_4 in Table I are similar to those in LiFePO_4 , indicating the structural stability of LiFePO_4 when Li de-intercalation occurs, which confirms that LiFePO_4 as a cathode material for rechargeable LIBs gains a long cycling lifetime.

3. RESULTS AND DISCUSSION

The calculated lattice parameters and atomic coordinates for $\text{LiFe}_{1/4}\text{Mn}_{1/4}\text{Co}_{1/4}\text{Ni}_{1/4}\text{PO}_4$ and $\text{Fe}_{1/4}\text{Mn}_{1/4}\text{Co}_{1/4}\text{Ni}_{1/4}\text{PO}_4$ are listed in Table I. As seen in Table I, ' a ' and ' b ' of $\text{LiFe}_{1/4}\text{Mn}_{1/4}\text{Co}_{1/4}\text{Ni}_{1/4}\text{PO}_4$ decrease by 0.2% and 0.2% compared with the experimental values, respectively, and ' c ' increases by 1.3% and the calculated volume increases by 0.9%. Thus, two structures are very similar. In addition, this is also the case between $\text{Fe}_{1/4}\text{Mn}_{1/4}\text{Co}_{1/4}\text{Ni}_{1/4}\text{PO}_4$ and $\text{LiFe}_{1/4}\text{Mn}_{1/4}\text{Co}_{1/4}\text{Ni}_{1/4}\text{PO}_4$, indicating the structural stability of the latter when Li de-intercalation occurs, which confirms that $\text{LiFe}_{1/4}\text{Mn}_{1/4}\text{Co}_{1/4}\text{Ni}_{1/4}\text{PO}_4$ as a cathode material for LIBs should benefit for a long cycling lifetime.

The corresponding average bond lengths and the bond angles of atoms in LiFePO_4 and FePO_4 , $\text{LiFe}_{1/4}\text{Mn}_{1/4}\text{Co}_{1/4}\text{Ni}_{1/4}\text{PO}_4$ and $\text{Fe}_{1/4}\text{Mn}_{1/4}\text{Co}_{1/4}\text{Ni}_{1/4}\text{PO}_4$ are calculated, which are also shown in Table I. In LiFePO_4 when Li de-intercalation occurs, the transition metal Fe is oxidized from Fe^{2+} to Fe^{3+} valence states, and the average bond length of Fe–O decreases by 4.4%, and P–O increases by 0.3%, and the average bond angles of O–Fe–O and O–P–O increase by 2.4% and 1.7%, respectively. In the case of $\text{LiFe}_{1/4}\text{Mn}_{1/4}\text{Co}_{1/4}\text{Ni}_{1/4}\text{PO}_4$ when Li de-intercalation occurs, Fe^{2+} , Mn^{2+} , Co^{2+} and Ni^{2+} is oxidized to Fe^{3+} , Mn^{3+} and Mn^{4+} , Co^{3+} and Ni^{3+} valence states, respectively, and the average bond lengths of Fe–O, Mn–O, Co–O, Ni–O and P–O decrease by 5.4%, 8.0%, 9.0%, 4.0% and 0.7%, respectively, and the average bond angles of O–Fe–O, O–Mn–O, O–Co–O, O–Ni–O and

Table I. Calculated lattice parameters and atomic coordinates, averaged bond lengths and the bond angles within $\text{LiFe}_{1/4}\text{Mn}_{1/4}\text{Co}_{1/4}\text{Ni}_{1/4}\text{PO}_4$, $\text{Fe}_{1/4}\text{Mn}_{1/4}\text{Co}_{1/4}\text{Ni}_{1/4}\text{PO}_4$, LiFePO_4 and FePO_4 with GGA.

	$\text{LiFe}_{1/4}\text{Mn}_{1/4}\text{Co}_{1/4}\text{Ni}_{1/4}\text{PO}_4$	$\text{Fe}_{1/4}\text{Mn}_{1/4}\text{Co}_{1/4}\text{Ni}_{1/4}\text{PO}_4$	LiFePO_4	FePO_4	LiFePO_4 (Expt. ³¹)
a (Å)	10.311	9.721	10.056	9.780	10.332
b (Å)	5.998	5.669	5.836	5.562	6.011
c (Å)	4.755	4.727	4.711	4.681	4.692
V (Å ³)	294.067	260.497	276.434	254.629	291.400
Li (4a)	(0, 0, 0)		(0, 0, 0)		(0, 0, 0)
Fe (4c)	(0.274, 1/4, 0.988)	(0.273, 1/4, 0.945)	(0.270, 1/4, 0.988)	(0.271, 1/4, 0.953)	(0.280, 1/4, 0.991)
P (4c)	(0.104, 1/4, 0.416)	(0.94, 1/4, 0.391)	(0.095, 1/4, 0.419)	(0.091, 1/4, 0.398)	(0.095, 1/4, 0.420)
O ₁ (4c)	(0.108, 1/4, 0.741)	(0.115, 1/4, 0.709)	(0.100, 1/4, 0.747)	(0.111, 1/4, 0.721)	(0.095, 1/4, 0.751)
O ₂ (4c)	(0.446, 1/4, 0.210)	(0.432, 1/4, 0.180)	(0.450, 1/4, 0.200)	(0.439, 1/4, 0.177)	(0.449, 1/4, 0.209)
O ₃ (8d)	(0.174, 0.045, 0.268)	(0.167, 0.041, 0.219)	(0.167, 0.039, 0.271)	(0.171, 0.036, 0.236)	(0.169, 0.046, 0.280)
Fe-O (Å)	2.081	1.969	2.069	1.977	
Mn-O (Å)	2.197	2.021			
Co-O (Å)	2.169	1.973			
Ni-O (Å)	2.129	2.043			
P-O (Å)	1.581	1.570	1.581	1.585	
O-Fe-O (°)	88.218	89.773	88.109	90.227	
O-Mn-O (°)	86.296	90.057			
O-Co-O (°)	86.124	90.514			
O-Ni-O (°)	88.159	90.295			
O-P-O (°)	104.718	105.928	104.090	105.875	

O–P–O increase by 1.8%, 4.4%, 5.1%, 2.4% and 1.2%, respectively. It is obvious that FeO_6 and NiO_6 octahedra are less distorted than MnO_6 and CoO_6 octahedra. The distortion in O–Mn–O angle would not seem to be a result of Mn doping into the LiFePO_4 host, but rather reflect Jahn-Teller distortion for octahedral coordination. This distortion in O–Mn–O angle also occurs on Li delithiation from $\text{Li}_2\text{Fe}_{0.875}\text{Mn}_{0.125}\text{SiO}_4$ to $\text{Li}_{0.875}\text{Fe}_{0.875}\text{Mn}_{0.125}\text{SiO}_4$.³⁷ As a comparison, our calculated average bond lengths are in accordance with the experimental results.³⁸ Thus, as for LiFePO_4 and $\text{LiFe}_{1/4}\text{Mn}_{1/4}\text{Co}_{1/4}\text{Ni}_{1/4}\text{PO}_4$ when Li de-intercalation occurs, the decreases in the average bond lengths of Fe–O, Mn–O, Co–O and Ni–O are due to the so-called rehybridization shift,³⁹ which occur in the transition metal ligand bond at high levels of oxidation in order to reduce the effect of valent change on the transition metal site. However, the average bond lengths of P–O are almost unchanged, implying the bonding nature between P and O atoms remains unchangeable during the delithiation-lithiation process. Thus, it is obvious that both $\text{LiFe}_{1/4}\text{Mn}_{1/4}\text{Co}_{1/4}\text{Ni}_{1/4}\text{PO}_4$ and LiFePO_4 show little structural distortions during Li de-intercalation, and this structural stability is actually the consequence of a strong covalent P–O bond.

The electron density difference diagrams of (001) surfaces of FePO_4 , LiFePO_4 , $\text{Fe}_{1/4}\text{Mn}_{1/4}\text{Co}_{1/4}\text{Ni}_{1/4}\text{PO}_4$, and $\text{LiFe}_{1/4}\text{Mn}_{1/4}\text{Co}_{1/4}\text{Ni}_{1/4}\text{PO}_4$ are shown in Figure 2. The gray balls denote Fe atoms. The red and blue regions denote the electron accumulation and loss. As shown in Figure 2, for $\text{Fe}_{1/4}\text{Mn}_{1/4}\text{Co}_{1/4}\text{Ni}_{1/4}\text{PO}_4$ and FePO_4 , the change of the electron density near Fe atoms occurs obviously when Li intercalation, and the electron accumulation around Fe sites by the Li intercalation happens, which is accompanied by the transformation of Fe atoms from the Fe^{3+}

Fig. 2. The electron density difference diagrams of (001) surfaces of (a) FePO_4 , (b) LiFePO_4 , (c) $\text{Fe}_{1/4}\text{Mn}_{1/4}\text{Co}_{1/4}\text{Ni}_{1/4}\text{PO}_4$ and (d) $\text{LiFe}_{1/4}\text{Mn}_{1/4}\text{Co}_{1/4}\text{Ni}_{1/4}\text{PO}_4$. The gray balls denote Fe atoms. The red and blue regions denote the electron accumulation and loss.

($t_{2g}^3 e_g^2$) to the Fe^{2+} ($t_{2g}^4 e_g^2$). Oppositely, Li de-intercalation in LiFePO_4 and $\text{LiFe}_{1/4}\text{Mn}_{1/4}\text{Co}_{1/4}\text{Ni}_{1/4}\text{PO}_4$ implies a systematic depletion of electron in the t_{2g} band.

The density of states (DOS) and partial density of states (PDOS) for LiFePO_4 , FePO_4 and Fe-3d states calculated are shown in Figure 3. As shown in Figure 3, LiFePO_4

Fig. 3. DOS and PDOS for LiFePO_4 , FePO_4 and Fe-3d states calculated with GGA. The Fermi level (vertical dotted line) is set to zero.

possesses a band gap (E_g) of 1.06 eV around the Fermi level E_F , being larger than calculated $E_g = 0.53$ eV,⁴⁰ and close to calculated E_g of 1.08 eV.⁴¹ Therefore, LiFePO_4 is a semiconductor with low electronic conductivity (our experimental value is $5.86 \times 10^{-9} \text{ S cm}^{-1}$),¹⁴ being much lower than that of commercial LiCoO_2 ($\sim 10^{-3} \text{ S cm}^{-1}$) cathode material.⁴² This decreases the discharge capacity upon cycling, as observed by us earlier for LiFePO_4 , where the discharge capacity loss over the first 30 cycles is $\sim 15\%$.⁷ As for LiFePO_4 , the valence band lies in the range from -11.85 to 0.00 eV formed by hybridization of $\text{Fe } 3d$ -states, $\text{P } 3p$ -states and $\text{O } 2p$ -states. The conduction bands are mainly made up from Fe-3d states and the two bands are separated by E_g around E_F . The PDOS of Fe-3d states demonstrates that the narrow bands near E_F can be assigned to Fe-3d bands. We observed the two main bands, one is from 1.26 to 2.71 eV corresponding to the conduction band with an e_g characteristics, and the other is from -1.66 to 0.00 eV, relating to the valence band with a t_{2g} characteristic. The above results show a typical Fe^{2+} state in LiFePO_4 .

The bonding nature for Li-intercalation into the host structures can be studied by comparing DOS of delithiated-lithiated phases. Since there is a strong bonding among Fe-3d , P-3p and O-2p states of FePO_4 , some metallic characteristics are present. When Li is intercalated, P-3p and O-2p states are shifted to the left with respect to E_F , leading to hybridization among Li-2s , P-3p and O-2p states. Fe-3d states are shifted left compared with E_F . Thus, the Li intercalation into the host structures is responsible for the metal-semiconductor transition of FePO_4 .

DOS and PDOS for $\text{LiFe}_{1/4}\text{Mn}_{1/4}\text{Co}_{1/4}\text{Ni}_{1/4}\text{PO}_4$, $\text{Fe}_{1/4}\text{Mn}_{1/4}\text{Co}_{1/4}\text{Ni}_{1/4}\text{PO}_4$, and related Fe-3d , Mn-3d , Co-3d and Ni-3d states are shown in Figure 4. There is a strong bonding among Fe-3d , Mn-3d , Co-3d , Ni-3d , P-3p and O-2p states in $\text{Fe}_{1/4}\text{Mn}_{1/4}\text{Co}_{1/4}\text{Ni}_{1/4}\text{PO}_4$, showing metallic characteristics. When Li is intercalated, the P-3p and O-2p states are shifted left with respect to E_F ,

Fig. 4. DOS and PDOS for (a) $\text{LiFe}_{1/4}\text{Mn}_{1/4}\text{Co}_{1/4}\text{Ni}_{1/4}\text{PO}_4$, (b) $\text{Fe}_{1/4}\text{Mn}_{1/4}\text{Co}_{1/4}\text{Ni}_{1/4}\text{PO}_4$, and related Fe-3d states, Mn-3d states, Co-3d states and Ni-3d states calculated with GGA. The Fermi level (vertical dotted line) is set to zero.

resulting in hybridization among Li-2s , P-3p and O-2p states. Fe-3d and Ni-3d states are shifted left too. Mn-3d , Co-3d and Ni-3d states form a band localized within the band gap, which is formed by Fe-3d states located below and above E_F , also displaying metallic characteristics of $\text{LiFe}_{1/4}\text{Mn}_{1/4}\text{Co}_{1/4}\text{Ni}_{1/4}\text{PO}_4$. Note that Mn-3d states play a key role in them.

4. CONCLUSIONS

Electronic and atomic structures of $\text{LiFe}_{1/4}\text{Mn}_{1/4}\text{Co}_{1/4}\text{Ni}_{1/4}\text{PO}_4$ and LiFePO_4 were investigated by using the first principles DFT. It is found that LiFePO_4 is a semiconductor with a band gap of 1.06 eV while $\text{LiFe}_{1/4}\text{Mn}_{1/4}\text{Co}_{1/4}\text{Ni}_{1/4}\text{PO}_4$ displays a metallic characteristic by filling the band gap with Mn-3d , Co-3d and Ni-3d states, implying an improvement in the electronic conductivity of $\text{LiFe}_{1/4}\text{Mn}_{1/4}\text{Co}_{1/4}\text{Ni}_{1/4}\text{PO}_4$. The doped material is expected to be promising cathode material for rechargeable LIBs.

Acknowledgments: The authors acknowledge the financial supports from The Project Sponsored by the Scientific Research Foundation for the Returned Overseas Chinese Scholars, State Education Ministry; International Science and Technology Cooperation Plan, Science and Technology Bureau of Changchun City (Grant No. 11GH01).

References and Notes

1. J. M. Tarascon and M. Armand, *Nature* 414, 359 (2001).
2. R. Cai, T. Yuan, R. Ran, X. Q. Liu, and Z. P. Shao, *Int. J. Energ. Res.* 35, 68 (2010).
3. S. Santhanagopalan and R. E. White, *Int. J. Energ. Res.* 34, 152 (2010).
4. D. P. Abraham, D. W. Dees, J. Christophersen, C. Ho, and A. N. Jansen, *Int. J. Energ. Res.* 34, 190 (2010).
5. A. K. Padhi, K. S. Nanjundaswamy, and J. B. Goodenough, *J. Electrochem. Soc.* 144, 1188 (1997).
6. L. N. Wang, Z. C. Li, H. J. Xu, and K. L. Zhang, *J. Phys. Chem. C* 112, 308 (2008).
7. B. Jin and H. B. Gu, *Solid State Ionics* 178, 1907 (2008).
8. C. A. J. Fisher, V. M. H. Prieto, and M. S. Islam, *Chem. Mater.* 20, 5907 (2008).
9. C. Delacourt, P. Poizot, M. Morcrette, J. M. Tarascon, and C. Masquelier, *Chem. Mater.* 16, 93 (2004).
10. N. N. Bramnik, K. Nikolowski, C. Baehtz, K. G. Bramnik, and H. Ehrenberg, *Chem. Mater.* 19, 908 (2007).
11. A. R. Armstrong, N. Kuganathan, M. S. Islam, and P. G. Bruce, *J. Am. Chem. Soc.* 133, 13031 (2011).
12. H. Yang, X. L. Wu, M. H. Cao, and Y. G. Guo, *J. Phys. Chem. C* 113, 3345 (2009).
13. E. M. Jin, B. Jin, D. K. Jun, K. H. Park, H. B. Gu, and K. W. Kim, *J. Power Sources* 178, 801 (2008).
14. B. Jin, E. M. Jin, K. H. Park, and H. B. Gu, *Electrochem. Commun.* 10, 1537 (2008).
15. A. Yamada, S. C. Chung, and K. Hinokuma, *J. Electrochem. Soc.* 148, A224 (2001).
16. A. Yamada, M. Hosoya, S. C. Chung, Y. Kudo, K. Hinokuma, K. Y. Liu, and Y. Nishi, *J. Power Sources* 119–121, 232 (2003).
17. D. Y. Wang, Z. X. Wang, X. J. Huang, and L. Q. Chen, *J. Power Sources* 146, 580 (2005).
18. J. J. Chen, M. J. Vacchio, S. J. Wang, N. Chernova, P. Y. Zavalij, and M. S. Whittingham, *Solid State Ionics* 178, 1676 (2008).
19. X. J. Wang, X. Q. Yu, H. Li, X. Q. Yang, J. McBreen, and X. J. Huang, *Electrochem. Commun.* 10, 1347 (2008).
20. K. W. Nam, X. J. Wang, W. S. Yoon, H. Li, X. J. Huang, O. Haas, J. M. Bai, and X. Q. Yang, *Electrochem. Commun.* 11, 913 (2009).
21. M. D. Bhatt, M. Cho, and K. Cho, *Appl. Surf. Sci.* 257, 1463 (2010).
22. G. H. Zhong, Y. L. Li, P. Yan, Z. Liu, M. H. Xie, and H. Q. Li, *J. Phys. Chem. C* 114, 3693 (2010).
23. Z. L. Wang, S. R. Sun, D. G. Xia, W. S. Chu, S. Zhang, and Z. Y. Wu, *J. Phys. Chem. C* 112, 17450 (2008).
24. J. L. Dodd, I. Halevy, and B. Fultz, *J. Phys. Chem. C* 111, 1563 (2007).
25. X. G. Xu, C. Li, J. X. Li, U. Kolb, F. Wu, and G. Chen, *J. Phys. Chem. B* 107, 11648 (2003).
26. L. Y. Hu, Z. H. Xiong, C. Y. Ouyang, S. Q. Shi, Y. H. Ji, M. S. Lei, Z. X. Wang, H. Li, X. J. Huang, and L. Q. Chen, *Phys. Rev. B* 71, 125433 (2005).
27. O. Le Bacq, A. Pasturel, and O. Bengone, *Phys. Rev. B* 69, 245107 (2004).
28. S. Q. Shi, D. S. Wang, S. Meng, L. Q. Chen, and X. J. Huang, *Phys. Rev. B* 67, 115130 (2003).
29. X. Duan, O. Warschkow, A. Soon, B. Delley, and C. Stampfl, *Phys. Rev. B* 81, 075430 (2010).
30. B. Delley, *J. Chem. Phys.* 92, 508 (1990).
31. B. Delley, *J. Chem. Phys.* 113, 7756 (2000).
32. J. P. Perdew, K. Burk, and M. Ernzerhof, *Phys. Rev. Lett.* 77, 3865 (1996).
33. J. P. Perdew and Y. Wang, *Phys. Rev. B* 45, 13244 (1992).
34. B. Delley, *Phys. Rev. B* 66, 155125 (2002).
35. H. J. Monkhorst and J. D. Pack, *Phys. Rev. B* 13, 5188 (1976).
36. V. Streltsov, E. L. Belokoneva, V. G. Tsirelson, and N. K. Hansen, *Acta Crystallogr. B* 49, 147 (1993).
37. P. Larsson, R. Ahuja, A. Liivat, and J. O. Thomas, *Comp. Mater. Sci.* 47, 678 (2010).
38. A. Losey, J. Rakovan, J. M. Hughes, C. A. Francis, and M. D. Dyar, *Can. Mineral.* 42, 1105 (2004).
39. F. Zhou, M. Cococcioni, C. A. Marainetti, D. Morgan, and G. Ceder, *Phys. Rev. B* 70, 235121 (2004).
40. S. Q. Shi, L. J. Liu, C. Y. Ouyang, D. S. Wang, Z. X. Wang, L. Q. Chen, and X. J. Huang, *Phys. Rev. B* 68, 195108 (2003).
41. Y. N. Xu, W. Y. Ching, and Y. M. Chiang, *J. Appl. Phys.* 95, 6583 (2004).
42. J. Molenda, A. Stoklosa, and T. Bak, *Solid State Ionics* 36, 53 (1989).

Received: 12 September 2012. Accepted: 7 December 2012.