Electronic Structure of Spinel-Type $\text{LiNi}_{1/2}\text{Ge}_{3/2}\text{O}_4$ and $\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$ as Positive Electrodes for Rechargeable Li-Ion Batteries Studied by First-Principles Density Functional Theory

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Abstract

Using first-principles density functional theory (DFT), we investigated the relationship between the electrochemical properties of the Li-containing spinel oxides $\text{LiNi}_{1/2}\text{Ge}_{3/2}\text{O}_4$ and $\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$ and their crystal and electronic structures in consideration of possible application of these materials as positive electrodes in rechargeable Li-ion batteries. $\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$ is known to exhibit excellent electrochemical performance, whereas $\text{LiNi}_{1/2}\text{Ge}_{3/2}\text{O}_4$ is electrochemically inactive. Thus, we

compared these compounds by DFT calculations. The calculated average intercalation voltage and migration energy of Li in $\text{LiNi}_{1/2}\text{Ge}_{3/2}\text{O}_4$ were found to be higher than those in $\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$, confirming the reported electrochemical inactivity of $\text{LiNi}_{1/2}\text{Ge}_{3/2}\text{O}_4$. A detailed study of electronic structure revealed that the strong ionic character of Ni–O bonds in $\text{LiNi}_{1/2}\text{Ge}_{3/2}\text{O}_4$ may be attributed to the inductive effect from the enhanced covalent character of Ge–O bonds.

Introduction

Spinel-type $\text{LiM}_x\text{Mn}_{2-x}\text{O}_4$ compounds ($\text{M} = \text{Fe}^{3+}$, Co^{3+} , Cu^{2+} , and Ni^{2+}) have attracted considerable attention as positive electrodes for rechargeable Li-ion batteries, owing to (1) their higher voltage, over 4.5 V versus Li^+/Li , than that of LiCoO_2 , LiNiO_2 , LiMn_2O_4 , and LiFePO_4 ; and (2) recent efforts toward improving electrolytes in order to increase the potential to around 5 V.[1-12] Among these compounds, $\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$ is especially promising because of its high discharge capacity, good cyclability, and dominant plateau at approximately 4.7 V; in contrast, the other materials exhibit two plateaus at approximately 4 and 5 V.[7-12] In $\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$, the electrochemical redox reaction at ~4.7 V is thought to proceed by electron transfer involving $\text{Ni}^{2+}/\text{Ni}^{4+}$ together with lithiation and delithiation.[11-12] Thus, one can envision new electrode compounds of the $\text{LiNi}_{1/2}\text{X}_{3/2}\text{O}_4$ family, in which electrochemically inert Mn^{4+} is

replaced with another tetravalent cation, X^{4+} . From this family of compounds, $\text{LiNi}_{1/2}\text{Ge}_{3/2}\text{O}_4$ is a promising candidate with cubic $P4_332$ symmetry and Ni/Ge = 1:3 at octahedral sites (see **Figure 1**).[13] However, Kawai *et al.* have reported that $\text{LiNi}_{1/2}\text{Ge}_{3/2}\text{O}_4$ is electrochemically inactive below 5.0 V vs. Li^+/Li . [3]

Plausible explanations for this electrochemical inertness are (1) high electrochemical voltage above 5.0 V, (2) poor Li-ion conductivity, and (3) poor electronic conductivity. In the present study, we revisited $\text{LiNi}_{1/2}\text{Ge}_{3/2}\text{O}_4$ as a candidate electrode material for Li-ion batteries, and used first-principles density functional theory (DFT) to investigate two of the material's properties for the first time : electrochemical voltage and Li migration. For comparison, we also investigated the crystal and electronic structures of $\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$.

Methods

The calculations were performed using the spin-polarized generalized gradient approximation (GGA-PBE) [14] and GGA + U [15,16] exchange-correlation functionals, with the plane-wave basis set and the projector-augmented wave method,[17,18] as implemented in the Vienna Ab-initio Simulation Package.[19,20] The effective U parameter value for d electrons of both Ni and Mn was determined to be 5.0 eV by

referring to a report on self-consistent calculation of U.[21] All the calculations were performed using a cubic unit cell with $P4_32$ symmetry,[13] which contains 8 formula units of $\text{Li}_x\text{Ni}_{1/2}\text{X}_{3/2}\text{O}_4$ ($\text{X} = \text{Ge}$ and Mn) with $3 \times 3 \times 3$ k-point meshes. The nudged elastic band (NEB) method was used to investigate the minimum energy pathways of the Li hop from one lattice position (8c site) to the adjacent 8c sites.[22,23] Details of the NEB method are described by Jonsson *et al.* [24]

Results and Discussion

Table 1 lists the calculated lattice parameters and average intercalation voltages (AIVs) [25] for $\text{LiNi}_{1/2}\text{Ge}_{3/2}\text{O}_4$ and $\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$. AIV was computed by using the following equation:

$$\text{AIV} = E(\text{LiNi}_{1/2}\text{M}_{3/2}\text{O}_4) - E(\text{Ni}_{1/2}\text{M}_{3/2}\text{O}_4) - E(\text{Li}) \quad (\text{M} = \text{Ge or Mn})$$

Here, $E(\text{X})$ is the total energy of compound X. By our DFT calculation, the cubic lattice parameters of $\text{LiNi}_{1/2}\text{Ge}_{3/2}\text{O}_4$ and $\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$ were slightly overestimated ($\sim 1.5\%$) in comparison with the reported experimental values; this is typical GGA + U error. The trend of the lattice parameters calculated by DFT agrees with experimentally observed trend: the lattice parameter of $\text{LiNi}_{1/2}\text{Ge}_{3/2}\text{O}_4$ is slightly larger than that of $\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$.

The calculated AIV of $\text{LiNi}_{1/2}\text{Ge}_{3/2}\text{O}_4$ (~ 4.9 V vs Li^+/Li) was much higher than that of $\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$ (~ 4.5 V). The reported discharge voltage for $\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$ is ~ 4.7 V,[27] which agrees well with the present slightly overestimated AIV. As mentioned in the introduction, $\text{LiNi}_{1/2}\text{Ge}_{3/2}\text{O}_4$ has been studied by cyclic voltammetry in the voltage range 2–5 V. Considering overvoltage and typical GGA + U error, electrochemical delithiation should occur above 5 V, a voltage at which currently known electrolyte solutions decompose. This might account for the electrochemical inactivity observed in the previous study.[3]

The migration energies of Li ions in $\text{LiNi}_{1/2}\text{Ge}_{3/2}\text{O}_4$ and $\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$ were calculated by the NEB method. The results show that the trajectory of the Li hop was straight along the {111} direction between two adjacent Li ions occupying tetrahedral 8c sites via an octahedral vacancy site between them. Note that two migration paths were calculated, in which Li ion passes through an octahedral 4b vacancy site (route A) or an octahedral 12d vacancy site (route B), as shown in **Figure 1 (b)**. Since route A (*i.e.*, the 8c-4b-8c path) cannot form a migration network, route B (*i.e.*, the 8c-12d-8c path) should directly correspond to the activation energy observed by conductivity measurement.

Figure 2 shows the calculated energy profiles; the highest energy barrier on each

path was located between the two tetrahedral sites, or at the octahedral vacancy (the 4b or 12d site). For both compounds, the energy barrier of route B was smaller than that of route A. In addition, migration energies varied with composition. As mentioned above, route B forms a three-dimensional continuous migration network in the lattice; hereinafter, we will consider this energy profile only, unless noted otherwise. The migration energy for $\text{LiNi}_{1/2}\text{Ge}_{3/2}\text{O}_4$ was around 0.47 eV, which was higher than that for LiNiMnO_4 (~0.32 eV). This 0.15 eV difference in migration energy corresponds to a large change in conductivity at room temperature, by a factor of 350 ($\exp(\Delta E/k_B T) \approx 350$ for $\Delta E = 0.15$ eV and $T = 298$ K). This finding from our calculation agrees well with the reported experimental results, in which a small ionic conductivity of $< 10^{-5}$ S/cm at room temperature was observed.[3] Therefore, the higher migration energy in $\text{LiNi}_{1/2}\text{Ge}_{3/2}\text{O}_4$ may also contribute to its electrochemical inertness.

As mentioned above, LiNiGeO_4 exhibited AIV and migration energy different from those of LiNiMnO_4 , though both compounds have similar crystal structure parameters (listed in Table 1). To clarify the origin of these different properties between LiNiGeO_4 and LiNiMnO_4 , their electronic structures were examined. **Table 2** lists the spin integral (SI) results at a radius of 1.40 Å for Ni, Ge, and Mn ions in each compound before and after delithiation. Note that SI corresponds to the total difference in electron spin (net

spin) for a given ion. SI is calculated as spin-up electrons minus spin-down electrons integrated over the radius of the ion core. The SI for Ni ions in $\text{LiNi}_{1/2}\text{Ge}_{3/2}\text{O}_4$ changed from 1.7 to 0 upon delithiation; this corresponds to the valence state of Ni ions changing from +2 ($t_{2g}^6e_g^2$) to +4 ($t_{2g}^6e_g^0$) with a low-spin configuration. In contrast, the SI of Ge ions was zero before and after delithiation. Therefore, electron transfer for delithiation takes place at Ni ions in only $\text{LiNi}_{1/2}\text{Ge}_{3/2}\text{O}_4$. A similar trend was observed in $\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$. However, looking in detail, we see that the difference in the SI of Ni in $\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$ was slightly smaller than the corresponding difference in Ni in $\text{LiNi}_{1/2}\text{Ge}_{3/2}\text{O}_4$. The SIs of Mn in $\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$ and $\text{Ni}_{1/2}\text{Mn}_{3/2}\text{O}_4$ were around 3.3 and 3.4, respectively, which corresponds to the valence state of +4 ($t_{2g}^3e_g^1$). The small difference in the SI of Mn before and after delithiation is discussed later in this paper.

To clarify the electron transfer reaction in the two compounds, the difference in electron density was calculated before and after delithiation in the (001) plane (**Figure 3**). Note that we used the same lattice parameter value for the delithiated and lithiated phases in the calculation of electron density distribution. As shown in the figure, large change in electron density was observed around Ni ions in $\text{LiNi}_{1/2}\text{Ge}_{3/2}\text{O}_4$, but no change in electron density was observed around Ge ions. These results agree with the results of the SI analysis. Moreover, upon delithiation, there was a small decrease in the

electron density around oxygen ions, indicating hybridization between Ni 3d and O 2p orbitals. Similarly, electron density around Ni and O ions was altered by delithiation in $\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$. However, a much larger amount of electrons was transferred around oxygen ions than Ni ions, and Mn ions were also involved in the electrochemical redistribution of electron density. As mentioned above, the slight increase of the SI of Mn ions upon delithiation originates not from the reduction of Mn ions, but from the partial oxidation of the neighboring O 2p band. On the one hand, these results imply stronger orbital hybridization between transition metal ions (Ni and Mn) and oxygen ions in $\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$ than that between Ni and O in $\text{LiNi}_{1/2}\text{Ge}_{3/2}\text{O}_4$, resulting in a lower electrochemical voltage in $\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$. On the other hand, the results indicate strong localization of the Ni 3d orbital (*i.e.*, strong ionicity of Ni ions), due to strong orbital hybridization between Ge and O ions in $\text{LiNi}_{1/2}\text{Ge}_{3/2}\text{O}_4$ as often seen in polyanionic compounds, such as LiFePO_4 .^[28] Hence, the higher AIV in $\text{LiNi}_{1/2}\text{Ge}_{3/2}\text{O}_4$ than in $\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$ can be explained by stronger ionicity of Ni ions, since the valence bands form a lower energy region. We infer that the relatively lower migration energy of Li in $\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$ is attributable to charge redistribution among Ni and Mn ions during Li hopping, as reported in our previous paper.^[23] In contrast, such a charge redistribution mechanism is less significant in $\text{LiNi}_{1/2}\text{Ge}_{3/2}\text{O}_4$ as a result of the strong

localization of the Ni 3d orbital, leading to higher migration energy of Li. Accordingly, the variation in electronic structure during electrochemical delithiation and Li hopping plays an important role in the electrochemical properties of spinel-type $\text{LiNi}_{1/2}\text{Ge}_{3/2}\text{O}_4$ and $\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$. Further study is needed, especially of the Li migration in these compounds, and we plan to investigate in detail the evolution of electronic structure during Li hopping in the near future.

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References

1. C. Sigala, D. Guyomard, A. Verbaere, Y. Piffard and M. Tournoux, *Solid State Ionics*, **81**, 167 (1995)
2. K. Amine, H. Tsukamoto, H. Yasuda and Y. Fujita, *J. Power Sources*, **68**, 604

(1997)

3. H. Kawai, M. Tabuchi, M. Nagata, H. Tsukamoto A. R. West, *J. Mater. Chem.*, **8**, 1273 (1998)
4. H. Kawai, M. Nagata, H. Tsukamoto and A. R. West, *Electrochim. Acta*, **45**, 315 (1999)
5. H. Kawai, M. Nagata, M. Tabuchi, H. Tsukamoto and A. R. West, *Chem. Mater.*, **10**, 3266 (1998)
6. H. Shigemura, H. Sakaebe, H. Kageyama, H. Kobayashi, A. R. West, R. Kanno, S. Morimoto, S. Nasu and M. Tabuchi, *J. Electrochem. Soc.*, **148**, A730 (2001)
7. Q. Zhong, A. Bonakdarpour, M. Zhang, Y. Gao and J. R. Dahn, *J. Electrochem. Soc.*, **144**, 205 (1997)
8. S. T. Myung, S. Komaba, N. Kumagai, H. Yashio, H. T. Chung, T. H. Cho, *Electrochim. Acta*, **47**, 2543 (2002)
9. Y. S. Lee, Y. K. Sun, S. Ota, T. Miyahara and M. Yoshino, *Electrochem. Commun.*, **4**, 989 (2002)
10. K. Kanamura, W. Hoshikawa and T. Umegaki, *J. Electrochem. Soc.*, **149**, A339 (2002)
11. T. Ohzuku, S. Takeda, M. Iwanaga, *J. Power Sources*, 81-82, 90 (1999)

12. H. Kawai, M. Nagata, H. Tukamoto, A. R. West, *J. Power Sources*, 81-82, 67 (1999)
13. K. Hirota, M. Ohtani, N. Mochida, A. Ohtsuka, *J. Ceram. Soc. Jpn*, 96, 92-96, (1988). The structural parameters are tabulated in ICSD dataset #68339.
14. J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Sing and C. Fiolhais, *Phys. Rev. B* **1992**, 46, 6671.
15. V. I. Anisimov, J. Zaanen, O. K. Andersen, *Phys. Rev. B*, **1991**, 44, 943.
16. A. I. Liechtenstein, V. I. Anisimov, J. Zaanen, *Phys. Rev. B* **1995**, 52, R5467.
17. P. E. Blöchl, *Phys. Rev. B* **1994**, 50, 17953.
18. G. Kresse, D. Joubert, *Phys. Rev. B* **1999**, 59, 1758.
19. G. Kresse, J. Furthmuller, *Phys. Rev. B* **1996**, 54, 11169.
20. G. Kresse, J. Furthmuller, *Comput. Mater. Sci.* **1996**, 6, 15.
21. F. Zhou, M. Cococcioni, C. A. Marianetti, D. Morgan, G. Ceder, *Phys. Rev. B* **2004**, 70, 235121.
22. B. Xu, S. Meng, *J. Power Sources*, 2010, 195, 4971
23. M. Nakayama, M. Kaneko, M. Wakihara, *Phys. Chem. Chem. Phys.* 14, 13963-13970 (2012)
24. (37) H. Jonsson, G. Mills, K. W. Jacobsen, B. J. Berne, in “Classical and Quantum

Dynamics in Condensed Phase Simulations; D. Chandler, D., B. J. Berne, G.

Ciccotti, D. F. Coker, Eds.; World Scientific: Singapore, 1998; p 385.

25. For example, G. Ceder, M. K. Aydinol, A. F. Kohan, Comput. Mater. Sci., 8 161
(1997)

26. D. Gryffroy, R. E. Vandenberghe, E. Legrand, Mater. Sci. Forum, 79, 785-790
(1991)

27. M. Jo, Y.-K. Lee, K. M. Kim, J. Cho, J. Electrochem. Soc. 157 A841-A845 (2010)

28. A. K. Padhi, K. S. Nanjundawamy, J. B. Goodenough, J. Electrochem. Soc. 1997,
144, 1188.

29. K. Momma and F. Izumi, J. Appl. Crystallogr., 2008, 41, 653.

Figure 1 (Color online) (a) Crystal structure of $\text{LiNi}_{1/2}\text{X}_{3/2}\text{O}_4$. ($\text{X} = \text{Ge}, \text{Ni}$). (b)

Three-dimensional diffusion network in spinel-type $\text{LiNi}_{1/2}\text{X}_{3/2}\text{O}_4$ with $P4_332$ symmetry.

4b and 12d vacancy sites served as migration pathways for Li ions, forming route A

(blue and green line) and route B (orange and green line), respectively.

Figure 2 Calculated energy profiles for the Li hopping in (a) LiNi_{1/2}Ge_{3/2}O₄ and (b) LiNi_{1/2}Mn_{3/2}O₄. Closed circles and open squares represent route A and B, respectively.

Figure 3 (Color online) Difference in electron density before and after delithiation in (a) $\text{LiNi}_{1/2}\text{Ge}_{3/2}\text{O}_4$ and (b) $\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$.

Table 1 Calculated and experimental cubic lattice parameters and averaged intercalation voltages (AIVs) for $\text{LiNi}_{1/2}\text{Ge}_{3/2}\text{O}_4$ and $\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$.

Sample	Cubic lattice parameter /Å		AIV /V
	Present calc.	Exp. reported	
$\text{LiNi}_{1/2}\text{Ge}_{3/2}\text{O}_4$	8.2936	8.181 [13]	4.91
$\text{Ni}_{1/2}\text{Ge}_{3/2}\text{O}_4$	8.1277		
$\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$	8.3090	8.17 [26]	4.58
$\text{Ni}_{1/2}\text{Mn}_{3/2}\text{O}_4$	8.1921		

Table 2 Change in spin integral before and after delithiation around Ni and X ions for $\text{LiNi}_{1/2}\text{X}_{3/2}\text{O}_4$ (X = Ge and Mn). The radius is set to 1.40 Å.

	X = Ge		X = Mn	
	Ni	Ge	Ni	Mn
$\text{LiNi}_{1/2}\text{X}_{3/2}\text{O}_4$	1.717	0	1.733	3.331
$\text{Ni}_{1/2}\text{X}_{3/2}\text{O}_4$	0.001	0	0.250	3.406