Density functional studies of olivine-type LiFePO_4 and NaFePO_4 as positive electrode materials for rechargeable lithium and sodium ion batteries

Masanobu Nakayama^{1,2,3,4*}, Shohei Yamada¹, Randy Jalem^{3,4}, and Toshihiro Kasuga⁵

¹*Department of Materials Science and Engineering, Nagoya Institute of Technology, Gokiso, Showa, Nagoya, Aichi 466-8555, Japan*

²*PRESTO, Japan Science and Technology Agency, PRESTO, 4-1-8 Honcho Kawaguchi, Saitama 332-0012, Japan*

³*Unit of Elements Strategy Initiative for Catalysts & Batteries (ESICB), Kyoto University, Katsura, Saikyo-ku, Kyoto 615-8520, Japan*

⁴*Global Research Center for Environment and Energy based on Nanomaterials Science (GREEN), National Institute of Materials Science (NIMS), 1-1 Namiki, Tsukuba, Ibaraki, 305-0044, Japan*

⁵*Department of Frontier Materials, Nagoya Institute of Technology, Gokiso, Showa, Nagoya, Aichi 466-8555, Japan*

E-mail: masanobu@nitech.ac.jp

Keywords: sodium ion battery; ion conductive ceramics; olivine-type structure; density functional theory

Abstract

Olivine-type LiFePO_4 is a positive electrode material for rechargeable Li ion batteries with

high power density (i.e. ability of fast charge–discharge rates). However, its Na alternative, olivine-type NaFePO₄, has a low power density as an electrode material for Na ion batteries. To understand the large difference of power density between LiFePO₄ and NaFePO₄, their ion and electron transport properties are investigated by first-principles density functional theory (DFT). In the present DFT studies, no significant difference in electronic migration energies in both bulk LiFePO₄ and NaFePO₄. On the other hand, the migration energy of sodium ion in NaFePO₄ is 0.05 eV higher than that of lithium ion in LiFePO₄, which may account for slow kinetics in NaFePO₄ electrode. Further studies of the phase stability and alkaline ion migration at the interfaces between the two phases of (Li/Na)FePO₄ and FePO₄ suggest that the difference in rate performance between LiFePO₄ and NaFePO₄ is related to the formation of this interface.

Introduction

Interest in olivine-type LiFePO₄ positive electrodes for rechargeable Li ion batteries has grown, because it is a cheap, abundant, and safe electrode material.[1-3] Several studies have reported the fast charge–discharge capability and high power density of LiFePO₄ derivative materials, which also exhibit stable cycling at a high current rate.[4-8] Thus, LiFePO₄ is expected to be used in batteries for hybrid and electric vehicles and portable devices. However, the limited availability of and access to Li reserves has led to economic uncertainty and speculation about the future use of Li ion

batteries, particularly for large batteries.[9-12] Therefore, research has intensively focused on Na ion batteries, which can offer a potential cost advantage because of the vast supply of Na. In this respect, the alternative Na electrode material, olivine-type NaFePO_4 , has been studied experimentally and theoretically.[13-23] However, olivine-type NaFePO_4 is not thermodynamically stable, and conventional solid-state reactions result in the formation of a maricite-type structure.[15, 24] Thus, the electrochemical ion exchange method is used to synthesize olivine-type NaFePO_4 compounds[13, 15, 18] NaFePO_4 has been prepared by electrochemical ion exchange of Li ions in LiFePO_4 with Na ions, and the rate performance of the same electrode composite sheet was compared. Therefore, the effects of morphology and the micro- or mesopore structure of the cathode composite were eliminated. The slow kinetics in NaFePO_4 may be caused by diffusion-driven resistance, namely the ion and electron transport properties, in solid-state electrodes. In particular, the ionic radius of Na^+ is larger than that of Li^+ , which could increase the migration energy because of the repulsion arising from electron overlap between surrounding ions during hopping.[25, 26] Zhu et al. reported that the diffusion coefficient of Na^+ is 1–2 orders of magnitude lower than that of Li^+ in the olivine-type FePO_4 structure.[18] To understand the difference in the rate performance between LiFePO_4 and NaFePO_4 arising from ion and

electron migration, we performed first-principles density functional theory (DFT) calculations for both compounds.

Computational method

All the first-principles DFT calculations were performed with the Vienna Ab Initio Simulation Package[27, 28] using the modified Perdew-Burke-Ernzerhof generalized gradient approximation (PBEsol-GGA)[29, 30] and the projector-augmented wave (PAW) method[31]. Onsite Coulomb correction (GGA+ U) was included to describe the localized electronic states of Fe 3d in mixed-valence rare earth metals. U was set to 4.0 eV for the Fe 3d states, according to the literature.[32, 33] A spin polarization calculation was used. A kinetic cutoff energy of 500 eV, and $5 \times 5 \times 3$ k -point meshes in the AFePO₄ unit cell (28 atoms, A = Li or Na) were found by a convergence test (<3 meV/AFePO₄). Because the band gaps of both compounds were underestimated, which is typical of the GGA+ U functional[34], we used the Heyd-Scuseria-Ernzerhof (HSE06) hybrid functional to estimate the band gaps, and we calculated the intercalation voltages of LiFePO₄ and NaFePO₄ from the total energies of two end compositions before and after alkaline ion removal and metallic Li and Na. The details are described in the references [35, 36].

The energy profiles for the localized hole (polaron) hopping to the nearest

neighbor Fe site in the AFePO_4 cell were calculated by adapting the method used in Ref. [37]. First, the total energies and relaxed internal configurations of the local energy minima, q_i and q_f , in which a localized electron was positioned at one of the adjacent Fe ions, were calculated. Because the polaron hopping energy corresponds to the sequential variation of the local lattice distortion between the two configurations of q_i and q_f , it was assumed that the migration path could be linearized from the two configurations. The total energy calculation was performed for each intermediate configuration. The nudged elastic band (NEB) method[38] was used to investigate the minimum energy pathways of the alkaline ion jumps from one lattice position to adjacent sites. Both the hole and ion migration calculations were performed with $2 \times 2 \times 1$ (112 atoms) supercells ($2 \times 2 \times 2$ k -point meshes). An on-site Coulombic interaction, U term, was not included in the NEB calculations, because the numerous configurational degrees of freedoms of the hole arrangements along the ion migration path cause technical difficulties for convergence, as reported in the literatures.[39, 40]

Results and discussion

Table 1 lists the lattice parameters and intercalation voltages between AFePO_4 and FePO_4 calculated by the GGA+ U and HSE06 methods. The present computational

and previous experimental/computational lattice parameters and voltages agreed well. The voltage of $\text{LiFePO}_4/\text{FePO}_4$ was 0.41 V higher than that of $\text{NaFePO}_4/\text{FePO}_4$, which is slightly higher than the difference of 0.33 V in experimental anodic half-cell potential between Li^+/Li and Na^+/Na . Therefore, the lattice energies were slightly less stable for olivine-type NaFePO_4 compared with LiFePO_4 . [19]

Table 1. Computational voltages in the present study, and reported computational and experimental voltages for $\text{AFePO}_4/\text{FePO}_4$ (A = Li or Na).

	Voltage calculated in this study	Reported voltage	
	Computational (V)	Computational (V)	Experimental (V)
$\text{LiFePO}_4/\text{FePO}_4$	3.39 (HSE06) 3.52 (GGA+U)	3.45 (GGA+U) [19]	3.5 [1]
$\text{NaFePO}_4/\text{FePO}_4$	2.98 (HSE06) 2.90 (GGA+U)	3.08 (GGA+U) [19]	~3 [15]

Figures 1 (a) and (b) show the partial density of states (PDOS) around the Fermi level for olivine-type LiFePO_4 and NaFePO_4 , respectively, calculated by the

HSE06 functional. The electronic configuration of both compounds is similar. The localized Fe 3d bands form a valence band maximum and conduction band minimum, and the band gaps are larger than 3.8 eV in both compounds. Therefore, the intrinsic band conduction of electrons is negligible at room temperature because of the localization and wide band gap. Electronic conduction in LiFePO_4 mainly arises from localized electron/hole (polaron) hopping.[19] Polarons are created by the redox reaction of $\text{Fe}^{2+/3+}$ to maintain charge neutrality during electrochemical Li^+ or Na^+ removal (uptake). Figure 2 (a) shows the calculated energy profiles for localized hole (Fe^{3+}) jumps of ~ 0.2 eV for both compounds. The polaron migration energies are much smaller than the band gaps, and thus polaron migration is the dominant electron conduction mechanism. The similarity of the polaron migration energies of the two compounds indicates that the difference in rate performance does not stem from polaronic migration.

Figure 1. Partial density of states (PDOS) for (a) LiFePO_4 and (b) NaFePO_4 . PDOS is aligned so that the Fermi energy is zero.

Figure 2. Energy profiles for (a) polaron and (b) alkali ion migration in olivine-type AMPO₄ (A = Li or Na) using GGA+*U* and GGA functionals, respectively.

Alkali ion migration is another factor affecting the rate performance in batteries. NEB calculations were performed to evaluate the migration energies of alkali ions in LiFePO₄ and NaFePO₄. The GGA functional was used to avoid the effect of complicated polaron interactions. Figure 3 shows the migration trajectory of Na⁺ hopping in the NaFePO₄ bulk structure, which is similar to that of Li⁺ in LiFePO₄ (not shown). Li or Na ions at the octahedral site jump to the neighboring site via the tetrahedral vacancy site along the

<010> direction, forming one-dimensional pathway as reported in previous reports [6, 7, 41]. The migration energy profiles are shown in Figure 2(b), where the energy maximum is located at the center of migration path (tetrahedral vacancy). The migration energies are 0.29 and 0.35 eV in LiFePO₄ and NaFePO₄, respectively, which is consistent with previously reported values[19]. The migration energy of Na⁺ is slightly larger than that Li⁺, which may arise from the size effect of the larger ionic radius of 6-coordinate Na⁺ (1.02 Å) compared with Li⁺ (0.76 Å). According to the reference[6], the diffusion coefficient, D , can be expressed by migration energy, E_m , as follow,

$$D = a^2 \nu^* \exp\left(\frac{-E_m}{k_B T}\right) \quad (1)$$

where a , ν^* , k_B and T correspond to hopping distance, attempt frequency, Boltzmann constant, and absolute temperature, respectively. Therefore, the diffusion coefficient of Li, D_{Li} , reaches around 10-fold that of Na, D_{Na} , at room temperature from $D_{Li}/D_{Na} = (\exp(0.06 \text{ eV}/k_B T))$. Thus, above difference may account for the observed slow kinetics in Na insertion/removal reaction into/from Na_{1-x}FePO₄ electrode. Note that the diffusion distance, $\langle l \rangle$, is proportional to the square root of the diffusion coefficient, $\sqrt{D}$, according to random walk theory ($D = \langle l \rangle^2/(2t)$ for one dimensional diffusion[41]), the difference in migration distance is only a factor of 2.2 ($\sim\sqrt{10}$). In this respect, the effect of difference in diffusion coefficient between the two compounds (Figure 2(b))

may be small, if the particle size is small. Further study, such as finite element method (FEM), is required to estimate quantitatively the impact of migration energy difference between two compounds. In addition, the particle size effect is needed to evaluate experimentally to consider the blocking effect of anti-site defects in the one-dimensional diffusion tunnel as reported in the Ref.[41].

Figure 3 Trajectory of Na ions in the NaFePO₄ bulk structure calculated by the NEB method.

It has been reported that a major difference in the charge–discharge mechanism between compounds is the compositional range of the miscibility gap.[13, 42] A wide miscibility gap, which allows two phases to coexist, is observed experimentally between $x \sim 0.05$ and 0.9 in Li_{1-x}FePO₄ at room temperature, whereas it is between $x \sim 0.3$ and 1.0 in Na_{1-x}FePO₄. Therefore, early on in charging, a two-phase reaction occurs in the

$\text{Li}_{1-x}\text{FePO}_4$ electrode, whereas a solid-solution reaction proceeds in the $\text{Na}_{1-x}\text{FePO}_4$ electrode.

Figures 4 (a) and (b) display the formation energies of 193 types of Li/vacancy and Na/vacancy configurations in $\text{Li}_{1-x}\text{FePO}_4$ and $\text{Na}_{1-x}\text{FePO}_4$, respectively, calculated using the GGA+ U functional with the ramping method.[39] The formation energies, ΔE_f , are defined as

$$\Delta E_f(\text{A}_{1-x}\text{FePO}_4) = E_0(\text{A}_{1-x}\text{FePO}_4) - (1-x) E_0(\text{AFePO}_4) - x E_0(\text{FePO}_4) \quad (2)$$

where $E_0(\text{X})$ is the total energy of X. As shown in the figure, formation energies for $\text{Li}_{1-x}\text{FePO}_4$ are positive for all Li/vacancy configurations, in agreement with the experimental and computational studies of the two-phase reaction over almost the full range of x . [42-44] However, the formation energy minima for each of the compositions are negative in $\text{Na}_{1-x}\text{FePO}_4$. This indicates that the solid-solution mechanism or the formation of a superstructure at intermittent compositions arising from the Na/vacancy ordered arrangement occurs during charge–discharge reactions. At least, the Na ions and vacancies are miscible within the lattice in the intermittent composition. Recent experimental studies have clearly shown that the solid-solution reaction proceeds from $x = 0$ to ~ 0.3 and the two-phase reaction follows from $x \sim 0.3$ to ~ 1 in $\text{Na}_{1-x}\text{FePO}_4$ [13], indicating that the superstructure may form around $x \sim 1/3$. Our results show that the tie

lines of the convex hull, namely the formation energy path, is asymmetric with respect to composition; $\text{Na}_{1-x}\text{FePO}_4$ is more stable for $x < 0.5$ than for $x > 0.5$. However, present computation does not indicate clear evidence of reaction mechanism change at $x \sim 1/3$, such as formation of superstructure[17] due to limited number of sampling for Na/vacancy arrangements and ignoring its entropy effect. We plan to perform further studies of the phase stability of $\text{Na}_{1-x}\text{FePO}_4$ by using Monte Carlo simulation with the cluster expansion method to elucidate the Na/vacancy arrangement as a function of Na content.

Figure 4 Formation energies calculated with first-principles DFT for different (a) Li/vacancy and (b) Na/vacancy configurations in an $A_{1-x}FePO_4$ ($A = Li$ or Na) structure. Ground-state energies obtained from the present calculations are linked with solid lines.

Delmas *et al.* suggested a domino-cascade model to account for the fast charge–discharge performance of Li ion batteries, in which Li ions diffuse easily along the

$\langle 010 \rangle$ direction around the $\text{LiFePO}_4|\text{FePO}_4$ interface.[45] Therefore, the interfacial Li migration mechanism may be a dominant factor in Li transport in LiFePO_4 . To evaluate migration energy at the interface, we use $2 \times 2 \times 2$ supercell with a (100) $\text{LiFePO}_4|\text{FePO}_4$ interface (208 atoms) in this calculation (Figure 5 (b)) by sampling the Γ point due to limitations of our computational resources. Figure 5 (a) shows the trajectory of Li ions at the (010) interface of $\text{LiFePO}_4|\text{FePO}_4$ calculated by the NEB method. The corresponding trajectory of Na ions at the $\text{NaFePO}_4|\text{FePO}_4$ interface appears to agree with the results for $\text{LiFePO}_4|\text{FePO}_4$ (not shown). The migration path is similar to the alkali ion migration in bulk AFePO_4 (Figure 3). The corresponding migration energy profiles are shown in Figure 6 for the $\text{LiFePO}_4|\text{FePO}_4$ and $\text{NaFePO}_4|\text{FePO}_4$ interfaces. The migration energy profiles of the two compositions are similar, indicating the size effect of Li/Na ions in bulk polaron migration (Figure 2(a)) and bulk ion migration (Figure 2(b)) is small. However, the energy maximum is not located at the center of the migration path as in bulk alkali ion migration (Figure 2(b)), but at around the geometrical bottleneck formed by neighboring oxide ions. In addition, the migration energies drop considerably to around 0.12 eV for both compositions compared with the corresponding bulk migration energies of 0.29 to 0.35 eV (Figure 2(b)), which supports the explanation proposed by Delmas et al.[45] We infer that the

Coulombic interactions are the main reason for the large difference in the migration profile between the bulk and interfacial alkali ion hopping, as observed in spinel compounds.[46] In the bulk hopping mechanism, the energy maximum is located at the tetrahedral vacancy, where the short-range repulsive effect [25, 26] is smaller owing to the overlap of the electron clouds of the hopping ion and surrounding oxide ions (Figure 2(b)). Therefore, the instability of the transition state in the bulk hopping mechanism may originate from long-range Coulombic interactions according to the pure ionic crystal model. Note that our computational structure model, consisting of 208 atoms, is not able to reproduce the interfacial structure in terms of the thickness of the Li or Na-rich and -poor phases, because of the computational cost. Nevertheless, our results show that introducing an interface causes a large decrease in migration energies. In addition to the present computation, several $\text{LiFePO}_4|\text{FePO}_4$ boundary configurations have been proposed or observed experimentally that can be explained theoretically by the size effect of the ions.[47] Therefore, further studies are required including various interface model by such as molecular dynamics or kinetic Monte Carlo simulation using force field parameters that can deal with thousands of atoms.

Figure 5. (a) Calculated Li or Na ion migration trajectory at the $\text{AFePO}_4/\text{FePO}_4$ interface.

(b) Structure model for interfacial alkali ion migration in this study.

Figure 6 Calculated migration energy of alkali ions at the (010) interface for $\text{LiFePO}_4/\text{FePO}_4$ and $\text{NaFePO}_4/\text{FePO}_4$.

The phase stability (Figure 4) and interfacial migration mechanism (Figures 5 and 6) indicate that a fast charge–discharge mechanism occurs in $\text{Li}_{1-x}\text{FePO}_4$ electrodes owing to the interfacial Li ion migration mechanism ($E_m \sim 0.12$ eV) as proposed in the domino-cascade model, whereas a bulk conductivity mechanism is dominant in the $\text{Na}_{1-x}\text{FePO}_4$ electrode ($E_m \sim 0.35$ eV) because of the miscibility in terms of Na/vacancy arrangements in the lattice (Figure 4). For the comparison purpose, the migration energy of Na at intermediate composition of $\text{Na}_{0.5}\text{FePO}_4$ is estimated by NEB method using two stable Na/Vacancy configurations in Figure 4(b) as representative (See supporting information, Fig. S1). The evaluated migration energies are ~ 0.38 eV for both structure models, $\text{Na}_{0.5}\text{FePO}_4$, showing slight increase from ~ 0.35 eV of $\text{Na}_{0.1}\text{FePO}_4$ in Figure 2(b). Hence, the difference in migration energy of ~ 0.23 eV ($= 0.35 - 0.12$ eV), which corresponds to a rate difference of ~ 7600 ($= \exp(0.23 \text{ eV}/k_B T)$; see eqn.1), can reasonably account for the experimentally observed fast and slow kinetics of LiFePO_4 and NaFePO_4 electrodes, respectively[18]. Note that net volumetric Li transportation performance is smaller than above rate difference (~ 7600), since fast migration only occur at the interface.

In conclusion, our calculations for olivine-type LiFePO_4 and NaFePO_4 show no major difference in the band conduction mechanism (Figure 1), bulk polaron migration

mechanism (Figure 2 (a)), and bulk alkali ion migration mechanism (Figure 2 (b)). Therefore, the difference in alkali ion size is not a major factor controlling the rate performance of the charge–discharge reaction. However, the phase stability for olivine-type compounds indicates a two-phase reaction mechanism for the $\text{Li}_{1-x}\text{FePO}_4$ electrode and a solid-solution reaction mechanism for the $\text{Na}_{1-x}\text{FePO}_4$ electrode. Our results suggest that faster Li^+ migration at the interface than in the bulk originates from the two-phase reaction mechanism.[45] Accordingly, the formation of the interface in $\text{Li}_{1-x}\text{FePO}_4$ may play an important role in the fast charge–discharge properties of olivine-type electrodes. The ion exchange reaction at the electrode|electrolyte interface, which is beyond the scope of this paper, may also control the kinetics. To evaluate the contribution of the various factors quantitatively, precise assignment of the elemental electrochemical reaction is required.

Acknowledgement

The present work was partially supported by the PRESTO program of the Japan Science and Technology Agency and by the “Elements Strategy Initiative to Form Core Research Center” of the Ministry of Education, Culture, Sports, Science and Technology, Japan (since 2012).

References

- [1] A.K. Padhi, K.S. Nanjundaswamy, J.B. Goodenough, J. Electrochem. Soc. 144 (1997) 1188.
- [2] A. Yamada, Electrochemistry 71 (2003) 717.
- [3] M. Nakayama, K. Iizuka, H. Shiiba, S. Baba, M. Nogami, J. Ceram. Soc. Jpn. 119 (2011) 692.
- [4] B. Kang, G. Ceder, Nature 458 (2009) 190.
- [5] S.Y. Chung, J.T. Bloking, Y.M. Chiang, Nat. Mater. 1 (2002) 123.
- [6] D. Morgan, A. Van der Ven, G. Ceder, Electrochem. Solid State Lett. 7 (2004) A30.
- [7] M.S. Islam, D.J. Driscoll, C.A.J. Fisher, P.R. Slater, Chem. Mater. 17 (2005) 5085.
- [8] S.-i. Nishimura, G. Kobayashi, K. Ohoyama, R. Kanno, M. Yashima, A. Yamada, Nat. Mater. 7 (2008) 707.
- [9] K. Kubota, I. Ikeuchi, T. Nakayama, C. Takei, N. Yabuuchi, H. Shiiba, M. Nakayama, S. Komaba, J. Phys. Chem. C 119 (2015) 166.
- [10] M.M. Doeff, Y.P. Ma, S.J. Visco, L.C. Dejonghe, J. Electrochem. Soc. 140

(1993) L169.

[11] R. Alcantara, J.M. Jimenez-Mateos, P. Lavela, J.L. Tirado, *Electrochem. Commun.* 3 (2001) 639.

[12] J. Barker, M.Y. Saidi, J.L. Swoyer, *Electrochem. Solid State Lett.* 6 (2003) A1.

[13] J. Lu, S.C. Chung, S.-i. Nishimura, A. Yamada, *Chem. Mater.* 25 (2013) 4557.

[14] F. Boucher, J. Gaubicher, M. Cuisinier, D. Guyomard, P. Moreau, *J. Am. Chem. Soc.* 136 (2014) 9144.

[15] P. Moreau, D. Guyomard, J. Gaubicher, F. Boucher, *Chem. Mater.* 22 (2010) 4126.

[16] S.M. Oh, S.T. Myung, J. Hassoun, B. Scrosati, Y.K. Sun, *Electrochem. Commun.* 22 (2012) 149.

[17] M. Casas-Cabanas, V.V. Roddatis, D. Saurel, P. Kubiak, J. Carretero-González, V. Palomares, P. Serras, T. Rojo, *J. Mater. Chem.* 22 (2012) 17421.

[18] Y. Zhu, Y. Xu, Y. Liu, C. Luo, C. Wang, *Nanoscale* 5 (2013) 780.

[19] S.P. Ong, V.L. Chevrier, G. Hautier, A. Jain, C. Moore, S. Kim, X. Ma, G. Ceder, *Energy Environ. Sci.* 4 (2011) 3680.

[20] G.K.P. Dathar, D. Sheppard, K.J. Stevenson, G. Henkelman, *Chem. Mater.* 23 (2011) 4032.

- [21] H. Lin, Y. Wen, C. Zhang, L. Zhang, Y. Huang, B. Shan, R. Chen, *Solid State Commun.* 152 (2012) 999.
- [22] M. Dixit, H. Engel, R. Eitan, D. Aurbach, M.D. Levi, M. Kosa, D.T. Major, J. *Phys. Chem. C* 119 (2015) 15801.
- [23] M.S. Islam, C.A.J. Fisher, *Chem. Soc. Rev.* 43 (2014) 185.
- [24] J. Kim, D.-H. Seo, H. Kim, I. Park, J.-K. Yoo, S.-K. Jung, Y.-U. Park, W.A. Goddard Iii, K. Kang, *Energy Environ. Sci.* 8 (2015) 540.
- [25] I. Kishida, Y. Koyama, A. Kuwabara, T. Yamamoto, F. Oba, I. Tanaka, *J. Phys. Chem. B* 110 (2006) 8258.
- [26] M. Nakayama, H. Ikuta, Y. Uchimoto, M. Wakihara, Y. Terada, *Appl. Phys. Lett.* 81 (2002) 2977.
- [27] G. Kresse, J. Furthmuller, *Compt. Mater. Sci.* 6 (1996) 15.
- [28] G. Kresse, J. Furthmuller, *Phys. Rev. B* 54 (1996) 11169.
- [29] J.P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* 77 (1996) 3865.
- [30] J.P. Perdew, A. Ruzsinszky, G.I. Csonka, O.A. Vydrov, G.E. Scuseria, L.A. Constantin, X. Zhou, K. Burke, *Phys. Rev. Lett.* 100 (2008) 136406.
- [31] P.E. Blöchl, *Phys. Rev. B* 50 (1994) 17953.
- [32] M. Nakayama, M. Wakihara, *Electrochemistry* 76 (2008) 752.

- [33] O. Le Bacq, A. Pasturel, O. Bengone, Phys. Rev. B 69 (2004) 245107.
- [34] J.L.F. Da Silva, M.V. Ganduglia-Pirovano, J. Sauer, V. Bayer, G. Kresse, Phys. Rev. B 75 (2007) 045121.
- [35] V.L. Chevrier, S.P. Ong, R. Armiento, M.K.Y. Chan, G. Ceder, Phys. Rev. B 82 (2010) 075122.
- [36] M.K. Aydinol, A.F. Kohan, G. Ceder, K. Cho, J. Joannopoulos, Phys. Rev. B 56 (1997) 1354.
- [37] T. Maxisch, F. Zhou, G. Ceder, Phys. Rev. B 73 (2006) 104301.
- [38] G.M.a.K.M.J. H. Jonsson, World Scientific, Singapore (1998).
- [39] B. Meredig, A. Thompson, H.A. Hansen, C. Wolverton, A. van de Walle, Phys. Rev. B 82 (2010) 195128.
- [40] M. Liu, Z. Rong, R. Malik, P. Canepa, A. Jain, G. Ceder, K.A. Persson, Energy Environ. Sci. 8 (2015) 964.
- [41] R. Malik, D. Burch, M. Bazant, G. Ceder, Nano Lett. 10 (2010) 4123.
- [42] A. Yamada, H. Koizumi, S.I. Nishimura, N. Sonoyama, R. Kanno, M. Yonemura, T. Nakamura, Y. Kobayashi, Nat. Mater. 5 (2006) 357.
- [43] F. Zhou, C.A. Marianetti, M. Cococcioni, D. Morgan, G. Ceder, Phys. Rev. B 69 (2004) 235121.

- [44] F. Zhou, T. Maxisch, G. Ceder, *Phys. Rev. Lett.* 97 (2006) 155704.
- [45] C. Delmas, M. Maccario, L. Croguennec, F. Le Cras, F. Weill, *Nat. Mater.* 7 (2008) 665.
- [46] M. Nakayama, M. Kaneko, M. Wakihara, *Phys. Chem. Chem. Phys.* 14 (2012) 13963.
- [47] A. Abdellahi, O. Akyildiz, R. Malik, K. Thornton, G. Ceder, *J. Mater. Chem. A* 2 (2014) 15437.