Rationalization of Diversity in Spinel MgFe$_2$O$_4$ Surfaces

Haoyue Guo, Amy C. Marschilok, Kenneth J. Takeuchi, Esther S. Takeuchi, and Ping Liu*

1. Introduction

Iron ferrites (AFe$_2$O$_4$) have been recognized as one of the promising electrode materials for lithium ion batteries (LIBs) due to their earth abundance, high lithium storage, facile preparation method, and low toxicity. These materials include zinc ferrite (ZnFe$_2$O$_4$) and magnesium ferrite (MgFe$_2$O$_4$). Previously, by employing density functional theory (DFT) we mapped the surface diagram of MgFe$_2$O$_4$ and discovered the unique contributions of the surface facets to the initial lithiation, where Zn$^{2+}$ ions are the key to generate active sites and facilitate the Li$^+$ ion intercalation via the facile displacement from 8a to 16c sites. In the present study, we move from ZnFe$_2$O$_4$ to MgFe$_2$O$_4$, aiming to understand the effect of substitution of Zn$^{2+}$ for Mg$^{2+}$ on the structures and the preferential surface orientations of the pristine spinel ferrite using DFT. Such mechanistic insight at the atomic level can be of great importance to extract the tuning principle and enable the design or optimization of spinel structures as LIBs electrode materials. We note, the lithium adsorption on these surfaces, transport from the surface to the subsurface and intercalation in the bulk, which are important to describe the lithiation behaviors, are beyond the interest of current effort and will be studied separately.

It has been reported that MgFe$_2$O$_4$ can adopt spinel structures in three forms. One is the normal-spinel with an oxygen-cubic-close-packed array (Figure 1a). Like ZnFe$_2$O$_4$ the octahedral 16d sites are taken up by Fe$^{3+}$ ions and O$^{2-}$ ions are located at octahedral 32e sites, while all the 8a sites are occupied by Mg$^{2+}$ rather than Zn$^{2+}$ ions. In addition, the substitution of Zn$^{2+}$ for Mg$^{2+}$ can also enable the formation of MgFe$_2$O$_4$ via the mixed-spinel and inverse-spinel structures depending on the distribution of two metal cations between octahedral and tetrahedral sites. The mixed and inverse spinel structures correspond to partial (Figure 1b) or complete (Figure 1c) intermixing of Mg$^{2+}$ ions at the tetrahedral 8a sites and Fe$^{3+}$ ions at the octahedral 16d in the normal-spinel structures. The degree of inversion, $i$ as in (Mg$_{1-i}$Fe$_i$)$_{32e}$(Mg$_{2i}$Fe$_{1-i}$)$_{16d}$O$_{4}$, depends on the synthesis details, such as calcination temperature and preparation method.

The atomic structures and electronic properties of spinel electrode materials, such as Fe$_2$O$_3$ and ZnFe$_2$O$_4$ have been extensively studied using DFT. Comparatively, little attention has been made to mixed-spinel MgFe$_2$O$_4$ due to its structural complexity, where only the simplified normal-spinel structure was studied. In term of the surface, to our best knowledge, only one theoretical study has been reported on the MgFe$_2$O$_4$(1 1 1) surface with a specific termination; yet the origin for such choice of surface orientation and structure, rather than many other possibilities was not addressed.

Here, the surface diagram of MgFe$_2$O$_4$ in three spinel forms, normal-spinel, mixed-spinel, and inverse-spinel, were studied using DFT in order to understand what the preferred surface terminations of MgFe$_2$O$_4$ are and why these orientations are stable, which is essential to determine the capture of Li$^+$ and the initial transport of Li$^+$ from surface to bulk. The low-index surfaces, MgFe$_2$O$_4$(1 0 0), (1 1 0), (1 1 1), and high-index surface of (3 1 1) were considered. These specific surfaces were chosen for consideration based on prior the high resolution...
transmission electron microscope (HR-TEM) results, showing that the bulk-terminated (2 2 0), (1 1 1), (2 2 2), (3 1 1), (4 2 2), and (5 1 1) can be exposed facets of the MgFe$_2$O$_4$ crystal.

Further, the selected surface set for MgFe$_2$O$_4$ in this study is the same as that used previously for ZnFe$_2$O$_4$, which allows close comparison between the two systems and thus enhances the fundamental insight into the effect of substituting Zn$^{2+}$ for Mg$^{2+}$ on the surface diagram of iron ferrite. In addition, consideration of three types of spinel structures for MgFe$_2$O$_4$ provides the opportunity to pinpoint the effect associated with the distribution of A$^{2+}$ in the spinel structure. Indeed, our results rationalize the essential effect of the substitution of Zn$^{2+}$ for Mg$^{2+}$ in ferrite and provide new insights on how to control the shape of ferrite materials and thus tune the performances of LIBs.

2. Results and Discussion

2.1. MgFe$_2$O$_4$ Bulk and Surface

The supercell of MgFe$_2$O$_4$ bulk was constructed with the Fd$_{3}$m primitive cell containing eight formula units in normal-spinel, mixed-spinel, and inverse-spinel structures (Figure 1). According to the previous synchrotron X-ray powder diffraction (XPD) measurement$^{[11]}$ for the mixed-spinel structure, 75% of the tetrahedral 8a sites were chosen to be occupied by Fe$^{3+}$ ions and 25% of 8a sites are for Mg$^{2+}$ ions, while 62.5% for Fe$^{3+}$ ions and 37.5% for Mg$^{2+}$ ions were considered in the case of the octahedral 16d sites. As summarized in Table 1, the DFT-optimized lattice parameters and band gaps of three systems are in reasonable agreement with the values measured experimentally.$^{[6b, h, j, 8b, 9a, 13]}$

Various possible bulk-terminations of MgFe$_2$O$_4$(1 0 0), MgFe$_2$O$_4$(1 1 0), MgFe$_2$O$_4$(1 1 1), and MgFe$_2$O$_4$(3 1 1) surfaces in normal-spinel, mixed-spinel, and inverse-spinel structures were considered (Figures S1–S12, Supporting Information), where each termination was labeled by the corresponding composition in our notation. Additionally, due to the lowered symmetry as compared to the normal-spinel, the MgFe$_2$O$_4$(0 0 1) and MgFe$_2$O$_4$(0 1 1) surfaces were also considered for the mixed-spinel and the inverse-spinel. The corresponding surface phase diagrams (Figures 2–4) were determined based on the calculated $\zeta$ as a function of $\Delta \mu_{\text{Fe}}$ and $\Delta \mu_{\text{O}}$ (see the Experimental Section for details).

Among the four surfaces studied for normal-spinel MgFe$_2$O$_4$, the (1 0 0) and (3 1 1) surfaces were found to be stable under a range of chemical potentials for which normal-spinel MgFe$_2$O$_4$ bulk is stable (Figure 2). Specifically, in the Fe-rich and O-rich region, the stoichiometric Fe$_2$O$_3$-terminated MgFe$_2$O$_4$(1 0 0) or (1 0 0)-Fe$_2$O$_3$ in our notation is more stable than the (1 0 0) with the Mg terminations or (1 0 0)-Mg, which becomes stable in the Mg-rich region. In the Fe-poor and O-rich region, the MgO-terminated MgFe$_2$O$_4$(3 1 1) surface, (3 1 1)-MgO, is preferred; while at the Fe-intermediate region, the O-terminated MgFe$_2$O$_4$(3 1 1) surface, (3 1 1)-O$^2$, is favored. Yet, the preference for (3 1 1)-O$^2$ strongly depends on the chemical potential of O and Fe, which corresponds to a very small area in the surface phase diagram (Figure 2). In comparison, the other O-terminated MgFe$_2$O$_4$(3 1 1) surface, (3 1 1)-O$^1$, is the most likely surface configuration, which covers much larger area including most of the intermediate region. The difference between the two O-terminated surfaces is that the O$^1$-termination has a higher density of Mg$^{2+}$ exposed to the surface (Figure 2), which is the descriptor to surface stability as demonstrated later. Our results indicate that the (3 1 1) is likely the dominant facet in normal-spinel MgFe$_2$O$_4$, which aligns

![Figure 1. Structures of a) normal-spinel, b) mixed-spinel, c) inverse-spinel MgFe$_2$O$_4$.](image)

![Figure 2. Surface phase diagram and the corresponding structures of normal-spinel MgFe$_2$O$_4$.](image)

<table>
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<th>Table 1. The lattice parameters and band gaps of normal-spinel, mixed-spinel, and inverse-spinel MgFe$_2$O$_4$, in comparison with experimental data.</th>
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with the previous experiments using X-ray diffraction (XRD) and transmission electron microscope (TEM) techniques.\[9b,11\]

For the mixed-spinel MgFe\textsubscript{2}O\textsubscript{4}, the single orientation, \{1 0 0\} including (0 0 1) and (1 0 0), is favored under the condition that mixed-spinel MgFe\textsubscript{2}O\textsubscript{4} bulk is stable (Figure 3). Specifically, the stoichiometric FeO\textsubscript{2}-terminated MgFe\textsubscript{2}O\textsubscript{4}(0 0 1), (0 0 1)-FeO\textsubscript{2}, is stable under both Fe-rich and O-rich condition, which is in alignment with case in normal-spinel (Figure 2), while the MgFeO\textsubscript{2}-terminated MgFe\textsubscript{2}O\textsubscript{4}(1 0 0), (1 0 0)-Mg\textsubscript{1.5}Fe\textsubscript{1.5}O\textsubscript{4}, is preferred at the Fe-rich and O-intermediate/poor region, rather than (3 1 1)-O\textsuperscript{3} and (1 0 0)-Mg for the normal-spinel structure. The MgO\textsubscript{x}-terminated MgFe\textsubscript{2}O\textsubscript{4} (0 0 1), (0 0 1)-MgO\textsubscript{x}, rather than (3 1 1)-O\textsuperscript{3} seen for the normal spinel structure, is the most likely surface configuration, which covers the relatively large area in the phase diagram including the Fe-poor and large intermediate region. In comparison, the mixed-spinel MgFe\textsubscript{2}O\textsubscript{4}(1 1 0), (1 1 1), and (3 1 1) surfaces display higher cleavage energy \(\theta \approx 0.79-3.62\ \text{J m}^{-2}\), which measures the surface stability with respect to MgFe\textsubscript{2}O\textsubscript{4} bulk, and metallic Mg and Fe (see the Experimental Section for detail) and do not appear in the surface phase diagram.

The inverse-spinel MgFe\textsubscript{2}O\textsubscript{4}, displays the most diverse distribution in facet orientation under a range of chemical potentials for which inverse-spinel MgFe\textsubscript{2}O\textsubscript{4} bulk is stable, where the low-index surfaces (1 0 0), (0 0 1), (1 1 1), and high-index surface (3 1 1) can all be observed (Figure 4). The Fe- and O-rich region is dominated by the stoichiometric O-terminated MgFe\textsubscript{2}O\textsubscript{4}(3 1 1), (3 1 1)-O, which is different from that in both normal-spinel and mixed-spinel structures. The (1 0 0)-MgFeO\textsubscript{4} and (0 0 1)-Mg\textsubscript{2}FeO\textsubscript{4} surfaces are preferred at the Fe-intermediate or the O-intermediate region, similar to the mixed-spinel case. While the (1 1 1)-O surface covers the relatively large area in the phase diagram including the Fe-poor and extensive Fe- and O-intermediate regions.

According to the DFT calculations, the preferential facet orientation of MgFe\textsubscript{2}O\textsubscript{4} crystal is sensitive to the distribution of Mg\textsuperscript{2+} ions in the spinel structure. The facet-preference shifts from (1 0 0) and (3 1 1) in the normal-spinel, solely (1 0 0) in the mixed-spinel, to (1 0 0), (0 0 1), (1 1 1), and (3 1 1) in the inverse-spinel (Figures 2–4). Accordingly, the equilibrium shape of MgFe\textsubscript{2}O\textsubscript{4} crystal was estimated based on the Wulff’s theorem.\[15\] The MgFe\textsubscript{2}O\textsubscript{4} crystal is likely to adopt the truncated cubic shape surrounded with (1 1 1) (Figure 5a). While the perfect cube faceted by (1 1 1) is solely preferred for the mixed-spinel MgFe\textsubscript{2}O\textsubscript{4} (Figure 5b). For the inverse-spinel MgFe\textsubscript{2}O\textsubscript{4}, the octahedral shape surrounded by eight (1 1 1) planes seems to dominate (Figure 5c); while only in the Fe/O-rich region, a rhombic triacontahedron with thirty (3 1 1) planes can be favored (Figure 5d), which is likely to account for the spherical particle observed in experiments.\[2b,c,6b,9b] The DFT-predicted variation in crystal shape of MgFe\textsubscript{2}O\textsubscript{4} with the distribution of Mg\textsuperscript{2+} ions well explains the observed variety of facets in previous HR-TEM, based on the samples synthesized under different conditions.\[9b,11–12\]
2.2. Descriptor to Surface Stability of MgFe2O4

In our previous study on normal-spinel ZnFe2O4 surfaces, the low index surfaces of (1 1 0) with ZnFe2O4-termination, (1 1 1) with Zn-termination and O-termination are preferred in the surface phase diagram. It was found that the presence of stable FeO6 octahedral layer parallel to the surface is responsible for the high stability of ZnFe2O4(1 1 1) (Figure S13, Supporting Information). However, this does not seem to be the case for MgFe2O4. In this case, none of the above terminations are favored not only in normal-spinel MgFe2O4 by simply substituting Mg2+ for Zn2+, but also in the mixed-spinel and the inverse-spinel MgFe2O4. That is the variation of Mg2+ in AFe2O4 from Zn to Mg changes the descriptor for the surface stability.

Our DFT calculations show that the descriptor to the surface stability is not associated with the FeO6 octahedral layer, but the Mg2+ ions density exposed to the surface of MgFe2O4. The identification of Mg2+ ions density as the key descriptor is based on the statistics on densities of ions exposed for all the surfaces studied. Among all the ions in MgFe2O4, a clear linear relationship between the density of Mg2+ and the cleavage energy ϑ is observed (Figure 6), where the lower density of Mg2+ corresponds to the higher ϑ or the lower surface stability. While no clear correlation is observed between the surface stability and the densities of both Fe3+ and O2− ions (Figure S14, Supporting Information).

To understand the capability of Mg2+ in the stabilization of MgFe2O4 surfaces, the projected density of states (PDOS) of surface Fe3+, Mg2+, and O2− in MgFe2O4 was plotted (Figure 7). Common features in PDOS were observed despite of the diversity in surface diagram for normal (Figure 7a), mixed (Figure 7b), and inverse spinel (Figure 7c) structures. First, the conduction bands in MgFe2O4 are dominated by Fe 3d states and the valences bands are composed of Fe 3d states and O 2s2p states, as seen for the case of ZnFe2O4.[1] The difference emerges for the A2+ ions. In ZnFe2O4,[1] Zn 3d states dominate the states at approximately −5 eV below the Fermi level; while little contribution from Mg is observed. That is, when exposed to the surface, Mg is still in the oxidized divalent states due to the strong Mg–O binding. Mg2+ ions are more stable than Zn2+, Fe3+, and O2− ions on the surface. Due to the extremely high stability of Mg2+, the surface stability of MgFe2O4 is more dependent on the density of Mg2+ ions than the other ions as shown in Figure 6. In addition, such strong dependence on density of exposed Mg2+ ions likely overwhelm the contribution from the FeO6 octahedral layer parallel to the surface, which explains well the divergence of the surface phase diagram induced by substitution of Zn2+ for Mg2+, even though the same normal-spinel structure is adopted (Figure 2; Figure S13, Supporting Information). We note that the tuning principle of A2+ extracted above can vary from one case to the next. According to the present results, there are significant changes in structures of bulk and surfaces of AFe2O4 when moving from A = Zn to A = Mg, though both Zn2+ and Mg2+ ions are relatively stable. While more variations are likely observed by using less stable A2+, e.g., Cu2+, Mn2+, Co2+, where the situation can be more complicated and detailed investigation is necessary.

3. Conclusion

We employed DFT to study the surface structures and stability of the low-index surfaces, MgFe2O4(1 0 0), (1 1 0), (1 1 1), and high-index surface of (3 1 1). The consideration of three types of spinel conformations, normal-spinel, mixed-spinel, and inverse-spinel structures and the close comparison with ZnFe2O4 enable the gain of fundamental understanding on tuning capability of distribution and intrinsic property of A2+ ion toward the structures of spinel AFe2O4.

The variation in the distribution of Mg2+ ion within the spinel structure offers the shape-tuning of MgFe2O4 crystal. The normal-spinel MgFe2O4 favors (1 0 0) and (3 1 1) surface orientation under a range of chemical potentials for which the corresponding bulk is stable, leading to a truncated cubic morphology. In the case of mixed-spinel MgFe2O4, only the low-index surface (1 0 0) and (0 0 1) surfaces are stable, which likely favors the formation of a cubic particle; while the (1 0 0), (0 0 1), (1 1 1), and (3 1 1) surface are all preferred for the inverse-spinel MgFe2O4, and the octahedral shape can be the dominant. The variation of A2+ ion from Zn2+ to Mg2+ changes the descriptors to the surface stability, going from the presence of the FeO6 octahedral layer parallel to the surface to the density of highly stable Mg2+ ion exposed to the surface. Our results not only explain well the experimental observations on diverse morphologies of MgFe2O4, but also provide the guidance to tune the structures and likely the LIB behaviors of ferrite by substituting Zn2+ for Mg2+, which is difficult to achieve experimentally, but key to the rational design of spinel materials as LIBs materials.

4. Experimental Section

DFT Calculations: DFT implemented in the Vienna ab initio simulation package (VASP)[16] was employed. The spin-polarized DFT+U calculations[17] were carried out with the PAW potential[16b,18] using the PBE exchange–correlation functional[19] and a kinetic energy cutoff of 520 eV. A Hubbard U correction of Ueff = 5.3 eV was applied to the Fe d orbitals. This setup was successfully used to predict the structures and properties for other spinel systems according to our previous studies.[14–16] The Gaussian smearing method was used with the total energies converged better than 10−3 eV, and the final force on each atom is less than 0.02 eV Å−1. The first Brillouin zone was sampled on 3 × 3 × 1 k-mesh.

Surface Stability Calculations: The slab model was considered to describe various MgFe2O4 surfaces. The surface was modeled using
a $2 \times 2$ surface slab. To eliminate the effect introduced by different terminations on both ends of a slab surface, the same terminations were chosen. The number of layers included varied depending on the termination, making sure that the slab was terminated by the same surface termination. A 20 Å thick vacuum was added along the direction perpendicular to the surface to avoid the artificial interactions between the slabs. During geometry optimization, the top and bottom three layers were allowed to relax, while the rest were fixed at the bulk positions.

Following the previous studies,[1,7a,20] the stability of surface was determined by the surface energy defined as

$$\zeta = E_{\text{slab}} - \mu_{\text{Mg}} - y\mu_{\text{Fe}} - z\mu_{\text{O}}$$

(1)

where $E_{\text{slab}}$ is the total energy of MgFe$_2$O$_4$ surfaces. $\mu_{\text{Mg}}$, $\mu_{\text{Fe}}$, $\mu_{\text{O}}$ are the chemical potential of Mg, Fe, O, respectively, in Mg$_x$Fe$_y$O$_z$ surfaces; $S$ is the surface area of the slab.

The $\mu_{\text{Mg}}$, $\mu_{\text{Fe}}$, and $\mu_{\text{O}}$ has a range in which MgFe$_2$O$_4$ bulk is stable

$$\mu_{\text{Mg}} + 2\mu_{\text{Fe}} + 4\mu_{\text{O}} = E_{\text{MgFe}_2\text{O}_4}$$

(2)

$$\Delta\mu_{\text{Mg}} = \mu_{\text{Mg}} - \mu_{\text{Mg}}^\text{bulk} < 0$$

(3)

$$\Delta\mu_{\text{Fe}} = \mu_{\text{Fe}} - \mu_{\text{Fe}}^\text{bulk} < 0$$

(4)

$$\Delta\mu_{\text{O}} = \mu_{\text{O}} - \mu_{\text{O}}^\text{bulk} < 0$$

(5)

where $E_{\text{Mg}}$, $E_{\text{Fe}}$, $E_{\text{O}}$ are the total energy of metallic Mg bulk, metallic Fe bulk, and O in gaseous molecular O$_2$, respectively; $\Delta\mu_{\text{Mg}}$, $\Delta\mu_{\text{Fe}}$, and $\Delta\mu_{\text{O}}$ refer to

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**Figure 7.** Projected density of states (PDOS) of surface Mg$^{2+}$ (red), Fe$^{3+}$ (black), and O$^{2-}$ (blue) in a) normal-spinel, b) mixed-spinel, and c) inverse-spinel MgFe$_2$O$_4$. The stable facets in the phase diagram are marked with star.
the difference of chemical potential in the slab and in metallic bulk (Mg and Fe) or gas phase (O), at 0 K and 1 bar. Therefore, a more negative value indicates a Fe or O poor condition; while a value closes to 0 represents a Fe or O rich environment condition. This method has been proven previously, being able to describe well the experimental results of spinel metal oxide surfaces including Fe$_2$O$_3$, ZnFe$_2$O$_4$, and LiMn$_2$O$_4$.

Therefore, the surface energy was expressed as a function of $\Delta \mu_{\text{Fe}}$ and $\Delta \mu_{\text{O}}$:

$$\zeta = \vartheta - \frac{1}{2} \left( \frac{y}{2} - x \right) \Delta \mu_{\text{Fe}} + \left( \frac{y}{2} - x \right) \Delta \mu_{\text{O}}$$

(6)

$$\vartheta = E_{\text{slab}} - x E_{\text{Fe} \text{Mg}_{x-1} \text{O}_{y-1}} - \left( \frac{y}{2} - x \right) E_{\text{Fe}} - \left( \frac{y}{2} - x \right) E_{\text{O}}$$

(7)

where $\vartheta$ is the cleavage energy, a constant that measures the surface stability with respect to MgFe$_2$O$_4$ bulk, and metallic Mg, Fe. Based on the equations, the phase diagrams of various surfaces with different terminations of MgFe$_2$O$_4$ were determined.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

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density functional theory, ferrite, MgFe$_2$O$_4$, spinel, surface diagram

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