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A Density Functional Theory Study of the Ionic and Electronic Transport Mechanisms in LiFeBO₃ Battery Electrodes

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Supporting Information

ABSTRACT: Lithium iron borate is an attractive cathode material for Li-ion batteries due to its high specific capacity and low-cost, earth-abundant constituents. However, experiments have observed poor electrochemical performance due to the formation of an intermediate phase, that is, LiₓFeBO₃, which leads to large overvoltages at the beginning of charge. Using a convex-hull analysis, based on Hubbard-corrected density functional theory (DFT+U), we identify this intermediate phase as LiₓFeBO₃. Moreover, we show by means of the nudged elastic band (NEB) method, that the origin of these adverse electrochemical effects can be explained by an intrinsically low Li-ion and electron/hole-polaron mobility in LiₓFeBO₃ due to high activation barriers for both the ionic and electronic transport. These studies include the effects of the experimentally reported commensurate modulation. We have also investigated the Li-ion/hole diffusion through the interface between LiₓFeBO₃ and LiFeBO₃, which is found not to result in additional kinetic limitations from Li diffusion across the intraparticle interfaces. These findings suggest that the experimentally observed diminished performance associated with the formation of intermediate phases is linked to the intrinsically poor properties of the LiₓFeBO₃ phase rather than to the presence of interfaces between different phases.

1. INTRODUCTION

Lithium-ion batteries (LIBs) are now the dominating energy-storage medium for portable electronic devices and may provide an important step toward the improvement of storage of sustainable energy from intermittent sources such as wind, solar, and hydroelectric power in the form of large-scale battery grids enabling load leveling and peak shaving. In addition, LIBs provide the backbone for the growing demand for transportable energy storage in electric vehicles.

The heaviest electroactive component of a battery is the cathode and thus much research has focused on improving upon its energy density and power density. Among the most popular cathode materials is the layered transition-metal oxide, LiNi₁/₃Mn₁/₃Co₁/₃O₂ (NMC), which combines a high theoretical capacity of 278 mAh/g with excellent cyclability¹ but is limited by the toxicity and high cost of Co. A promising alternative to the layered transition-metal oxides are the transition-metal olivine-structured materials, such as LiFePO₄, which consists of earth-abundant, environmentally benign elements. However, LiFePO₄ suffers from a low rate capability resulting from low ionic and electronic conductivity, which can only be alleviated by down-sizing the particles of the active material, decreasing their volumetric energy density. Another member of the polyanionic structure class is lithium iron borate, LiFeBO₃, which enjoys a high theoretical specific capacity of 220 mAh/g and displays volume changes shown to be as small as 2% compared to 6.7% for the delithiation of LiFePO₄.² This significantly lowers the risk of the electrode material cracking during Li insertion and extraction, thereby preventing loss of contact between the active cathode material and current collector, resulting in an increase in the expected lifetime and overall battery performance. However, in many other applications of today’s battery systems an important requirement is fast charge and recharge properties. This puts severe restrictions on a number of available cathode materials, because both a low ionic and low electronic mobility will decrease the rate capability and achievable capacity of the cathode.³ Because many of the limitations on the rate capability of the cathode materials are caused by issues related to the electronic and ionic transport in the bulk and across external interfaces (e.g., carbon coating on an electrode) and internal interfaces (e.g., the interface between regions with different Li concentrations), improvements on these properties requires a detailed understanding of the reactions occurring at the interfaces at the atomic level. Such detailed insights can be accessed through advanced computational techniques, where, in particular, density functional theory (DFT)⁴,⁵ offers a compelling compromise between accuracy and computational cost, for instance, in studies involving fast screening of a wide range of materials properties as compared to conventional
experimental techniques. Not surprisingly, DFT studies have played a key role in determining the dominating transport mechanisms for Li ions (Li ions at Li-ion lattice sites) and holes (lattice sites where Li ions have been removed) in lithium transition-metal phosphates and borates, as well as for electrons and holes in lithium transition-metal phosphates and Li-air batteries.

In general, the formation of interfaces during charge/discharge has a large impact on electrochemical properties, such as rate capability, achievable capacity and voltage. In the case of LiFePO₄, the (de)lithiation mechanism in LiFePO₄ has been suggested to proceed via a two-phase reaction between the endmembers, Li₀.₉₈FePO₄ and Li₀.₀₂FePO₄. Because LiFePO₄ and LiFeBO₃ both have been shown to have their Li diffusion confined to channels (along the b-axis in LiFePO₄ and along the c-axis in LiFeBO₃), a natural question is whether the two compounds share the same (de)intercalation mechanism, that is, whether the (de)lithiation of LiFeBO₃ proceeds via a two-phase reaction. Galvanostatic intermittent titration technique (GITT) experiments on carbon-coated LiFePO₄ nanoparticles performed by Yamada et al. have revealed a continuous shift of diffusion peaks in the lattice parameters and a sloping OCV curve of LiFeBO₃, indicating a solid-solution-type behavior in the approximate Li-concentration range of 0.15 ≤ x ≤ 0.5 (that is, during the initial stage of discharge). Their GITT experiments and DFT studies suggested that in the Li-concentration range 0.5 ≤ x ≤ 1.0 one or more two-phase reactions occurred, which was unambiguously corroborated by Bo et al., who later reported indications or more two-phase reactions occurred, which was unambiguously corroborated by Bo et al.

Here, we first present a thermodynamic stability analysis of the possible compounds between the compositions FeBO₃ and LiFeBO₃, which reveals a stable intermediate phase at half lithiation, that is, at Li₀.₅FeBO₃. Second, the diffusion barriers of Li ions in FeBO₃, Li holes in LiFeBO₃, and Li ions in the most stable configuration of Li₀.₅FeBO₃ are calculated and a significant lowering of the diffusivity in Li₀.₅FeBO₃, as compared to the diffusivities in LiFeBO₃/FeBO₃, is predicted to take place.

Internal interfaces that may form during the initial-stage delithiation are also investigated and the Li-defect diffusion across the interfaces themselves is determined not to lower the overall Li transport in LiFeBO₃. Seo et al. calculated a 3.19 eV bandgap in LiFeBO₃, which is large enough to prevent the thermal activation of electrons or holes, and ascribed the electronic conduction to electron and hole polarons, that is, states where the excess charge is carried by a local distortion of the lattice. We prove the existence of these electron and hole polarons localizing on Fe ions and furthermore, the hopping mechanisms of these polarons in relevant phases of bulk LiFeBO₃ are investigated and we show that the most stable Li configuration in Li₀.₅FeBO₃ lowers the electronic mobility relative to both LiFeBO₃ and FeBO₃. These findings strongly suggest that the Li (de)intercalation in LiFeBO₃ is intrinsically impeded by the transport of Li ions and electron/hole polarons, in particular in the Li₀.₅FeBO₃ phase.

2. METHODOLOGY

2.1. The Crystal Structure of LiFeBO₃

Early experimental reports showed that lithium iron borate (LiFeBO₃) has a monoclinic crystal symmetry in which chains of edge-sharing FeO₄ trigonal bipyramids align along the [100] direction, and chains of LiO₄ tetrahedra in pairs run along the [001] direction with planar BO₃ groups connecting the edge-sharing FeO₄ chains. The DFT-optimized geometry of this structure is shown in Figure 1. X-ray diffraction studies by Janssen et al. revealed that a commensurately modulated superstructure exists in LiFeBO₃, which effectively doubles the unit cell along the α-axis and displaces the Li ions out of the trigonal bipyramidal equatorial planes toward the center of the four neighboring O ions and altering the crystal symmetry from C₂/c to C₂/c′(α0γ0)00 with α = 1/2 and γ = 0. Following Janssen et al., the modulation of LiFeBO₃ giving rise to the C₂/c′(α0γ0)00 crystal symmetry was also modeled here in a P₂₁/c crystal symmetry, and the lattice parameters and atomic positions used as a starting point for our structure optimizations of the modulated LiFeBO₃ were those in Table S7 reported by Janssen et al.: a = 10.3469 Å, b = 8.9209 Å, c = 10.2528 Å, and β = 90.878°. In order to assess the stability of the modulated (as modeled in the P₂₁/c symmetry) versus unmodulated (C₂/c symmetry) LiFeBO₃, calculations on unmodulated LiFeBO₃ were started with the lattice parameters reported by Janssen et al.: a = 5.1350 Å, b = 9.0437 Å, c = 10.2907 Å, β = 91.031°. Upon Li extraction (charge) of LiFeBO₃, the oxidation occurs on the Fe²⁺ ions, which become Fe³⁺ ions. The Fe ions are always determined to be in their high-spin state. Therefore, Fe in LiFeBO₃ is Fe²⁺ and Fe in FeBO₃ is Fe³⁺, possessing a magnetic moment of 4 and 5 μB, respectively.

2.2. Computational Methods

In this study, all structures were set up and analyzed using the Atomic Simulation Environment (ASE) package and relaxed to their ground
state by solving the electronic-structure problem within DFT. The Vienna Ab initio Simulation Package (VASP)\textsuperscript{23} was used in which plane waves were expanded up to a kinetic-energy cutoff of 500 eV and the projector-augmented-wave (PAW) method\textsuperscript{22} was employed to describe the atomic cores. In the PAW pseudopotentials, for Li, B, and O the 1s electrons were treated as core electrons and for Fe the electrons up to 3p (including 3p) were treated as core electrons. The exchange–correlation effects were described within the generalized-gradient approximation (GGA) by the Perdew–Burke–Ernzerhof (PBE) functional.\textsuperscript{23} For the determination of the partial occupancies, the tetrahedron method with Blöchl corrections\textsuperscript{24} were used and the electronic levels were smeared by 0.05 eV.

The incomplete cancellation of the electronic self-interaction in the GGA often leads to significant deviations from experimental results, in particular the band gap,\textsuperscript{25,26} which are due to the propensity of the self-interaction toward delocalizing the electrons, in particular for systems exhibiting a strong localization of the d-orbital electrons, as is the case of LiFeBO\textsubscript{3}. This problem has previously\textsuperscript{27,28} been alleviated by employing the Hubbard-U correction and following Seo et al.,\textsuperscript{29} a value of $U = 4.3$ eV was therefore applied on the 3d orbitals of Fe in LiFeBO\textsubscript{3}.

Three kinds of simulation cells were used. For the structural relaxation of the unit cell of LiFeBO\textsubscript{3}, the k-point sampling was performed using a Monkhorst–Pack\textsuperscript{28} (MP) mesh of $4 \times 2 \times 2$, for the $(2a,b,c)$ supercells a MP mesh of $2 \times 2 \times 2$ was used and for the $(a,b,2c)$ supercells a $4 \times 2 \times 1$ MP mesh was used. Structures were relaxed until all forces did not exceed 0.05 eV/Å using the FIRE minimization algorithm.\textsuperscript{27} The self-consistent solution to the Kohn–Sham equation was performed with an accuracy of 0.1 meV.

In our model, an electron (hole) polaron was simulated by adding (removing) an electron (hole) to the FeBO\textsubscript{3} (LiFeBO\textsubscript{3}) supercell having a compensating background charge in order to maintain charge neutrality. The symmetry of the system was broken by stretching (compressing) the Fe–O bonds for a particular Fe ion in the unit cell, around which the electron (hole) is expected to be localized. This approach enabled charge localization and lowered the computation time of the structural relaxations.

In order to determine the activation barriers of the Li-ion/ hole jumps and polaron hops, the nudged elastic band (NEB) method\textsuperscript{26} as implemented in ASE was employed with a total number of seven images, where the initial particle trajectory was created by linearly interpolating between the initial and final image. The energies and forces were calculated by VASP, and the forces were let to relax to the same threshold as for the structure relaxations (0.05 eV/Å).

3. RESULTS AND DISCUSSION

3.1. Optimized Lattice of LiFeBO\textsubscript{3}. Our DFT calculations on modulated LiFeBO\textsubscript{3} yields the optimized lattice parameters $a = 10.409$ Å, $b = 8.9953$ Å, $c = 10.324$ Å, and $\beta = 91.39^\circ$, and for unmodulated LiFeBO\textsubscript{3} the lattice parameters relaxed to $a = 5.1683$, $b = 9.1086$ Å, $c = 10.3485$ Å, and $\beta = 91.28^\circ$.\textsuperscript{30} The DFT calculations also reveal that the modulated phase of LiFeBO\textsubscript{3} is more stable than the unmodulated phase by 11 meV/f.u., agreeing well with the stability energy reported by Janssen et al.\textsuperscript{18} of 12 meV/f.u. Both sets of lattice parameters are in good agreement with experimental values \textsuperscript{18} (vide supra).

As Janssen et al.\textsuperscript{18} report, we find that the length of the apical Li–O bond (along the c-axis) in the LiO\textsubscript{4} tetrahedra is longer than the other Li–O bonds by approximately 0.1 Å in modulated LiFeBO\textsubscript{3}. Upon full delithiation yielding FeBO\textsubscript{3}, the lattice parameters relaxed to $a = 5.3078$ Å, $b = 8.9894$ Å, $c = 10.1876$ Å, and $\beta = 89.399^\circ$ resulting in a volume change from modulated LiFeBO\textsubscript{3} to FeBO\textsubscript{3} of 0.6 %.

3.2. Thermodynamics of Bulk LiFeBO\textsubscript{3}. Experimental and computational results by Yamada et al.\textsuperscript{4} and Bo et al.\textsuperscript{16} suggest the possible existence of partially lithiated phases. Using the convex-hull method,\textsuperscript{26} the phase stability of LiFeBO\textsubscript{3} at different Li concentrations were analyzed. In this method, the relative energy per formula unit at a given Li concentration, $x$, is given by

$$E_{\text{rel}}(x) = E_{\text{LiFeBO}_3} - xE_{\text{FeBO}_3} - (1 - x)E_{\text{LiBO}_3}$$

where $E_{\text{LiFeBO}_3}$ is the total energy obtained from DFT calculations for the respective structure per formula unit. The convex hull is constructed by connecting the most stable phases of the compound while ensuring that the curvature of the resulting curve is always positive. If the relative energy at a specific Li concentration is higher than the energy of the line joining the lowest-energy configurations at the neighboring Li concentrations (that is, the convex hull), the corresponding phase is unstable relative to a blend of the phases at the neighboring Li concentrations. This scenario would correspond to a two-phase reaction and would result in a plateau in the voltage profile. For the construction of the convex hull of LiFeBO\textsubscript{3}, all symmetry-invariant Li arrangements in the unit cell of unmodulated LiFeBO\textsubscript{3} were investigated: for $x = \{0, 1/8, 7/8, 1\}$, 1 combination exists, for $x = \{1/4, 3/8, 5/8, 3/4\}$, 7 combinations exist, and for $x = 1/2$, 14 combinations exist. These structures were then doubled in the $a$-direction, so as to resemble the size of the unit cell of modulated LiFeBO\textsubscript{3}, and fully relaxed. Naturally, the energy of the $a$-doubled unmodulated structures was twice the energy of the unmodulated unit-cell structure. The relative energies are shown in Figure 2a as black circles. Also, the Li configurations found in the unmodulated LiFeBO\textsubscript{3} structures were calculated with the modulation included, and these are shown in Figure 2a as black plusses. In order to extend the phase-stability model to include possible clustering of Li ions and holes, supercells were created by repeating the unit cell of unmodulated LiFeBO\textsubscript{3} in the $a$-direction. The selected Li configurations in these supercells were determined as those minimizing or maximizing the Coulomb repulsion between the Li ions, yielding an additional 14 structures (that is, two different structures for the seven intermediate configurations). The relative energies obtained from the supercell configurations of unmodulated LiFeBO\textsubscript{3} are included as red circles. Additionally, the Li configurations found in unmodulated LiFeBO\textsubscript{3} structures maximizing/minimizing the Coulomb repulsion were calculated with the modulation included, and these are shown in Figure 2a as red plusses. Figure 2b shows the profile for the open-circuit voltage (OCV) calculated by

$$U_{\text{OCV}}(x) = -\frac{E_{\text{LiFeBO}_3} - E_{\text{LiBO}_3} - (x_2 - x_1)E_{\text{Li}(s)}}{(x_2 - x_1)e}, \quad x_1 < x < x_2$$

where the energies, $E_{\text{LiFeBO}_3}$ are calculated using DFT and $E_{\text{Li}(s)}$ indicates that all voltages are calculated with respect to the Li-metal electrode.
Bo et al.\textsuperscript{16} that the modulation is lost in the delithiated phase with the same Li distribution. This tallies well with the suggestion of Yamada et al.\textsuperscript{2} that the modulated symmetry-inequivalent structure relaxes to that of the unmodulated phase. Li ions are distributed such that the Coulomb repulsion is minimized or maximizing the Coulomb repulsion, indicated by red markers, calculated by eq 1. The convex hull is indicated by the blue dashed line. The voltage profile calculated by eq 2 using the convex-hull energies in (a) is shown as a blue line and the equilibrium potential, $U_{\text{eq}} = E_{\text{FeBO}_3} - (E_{\text{LiBO}_3} + 16E_{\text{Li}^+})$, is shown as a black dashed line.

The convex-hull construction in Figure 2a shows that the lowest-energy Li configuration for the phases having Li concentration of $x = 0.0, 0.25, 0.375, 0.5$, and $0.625$ is obtained from an $a$-doubled unit-cell structure. In the case of $x = 0.125$, the lowest-energy Li configuration is obtained from an unmodulated unit-cell structure doubled in the $a$-direction, whereas for $x = 0.875$, the lowest-energy Li configuration is obtained from a modulated structure, though in both cases the Li ions are distributed such that the Coulomb repulsion between the Li ions is minimized. At the lowest concentration, the modulated symmetry-inequivalent structure relaxes to that of the unmodulated one. It is also noteworthy, that it is primarily for Li concentrations of $x > 0.5$ where the modulated structure is more stable than the unmodulated structure having the same Li distribution. This tallies well with the suggestion of Bo et al.\textsuperscript{16} that the modulation is lost in the delithiated phase and in other Li-deficient phases. The half-lithiated phase, $\text{Li}_{0.5}\text{FeBO}_3$, has the highest stability relative to the other calculated phases. The $\text{Li}_{0.75}\text{FeBO}_3$ phase predicted to be stable by Yamada et al.\textsuperscript{2} is also predicted to be stable in our model, whereas the phase at $\text{Li}_{0.5}\text{FeBO}_3$ and $\text{Li}_{0.75}\text{FeBO}_3$ is not. This is reflected in the voltage profile in Figure 2b, where three plateaus are seen, one at $3.26$ V for $0.0 < x < 0.5$, one at $2.93$ V for $0.5 < x < 0.75$, and one at $2.90$ V for $0.75 < x < 1.0$ together with an equilibrium voltage of $3.08$ V (dashed line), which compares well with experimental values of about $3.0$ V.\textsuperscript{7} The bending of the convex hull due to the stable phase at $x = 0.75$ results in a plateau splitting of $0.05$ V between the voltage plateaus at $0.5 < x < 0.75$ and $0.75 < x < 1.0$, a voltage difference that is likely to be detectable only in very slow GITT experiments.

The crystal structure of the lowest-energy configuration in the half-lithiated phase is shown in Figure 3 and the positions of the Li ions in the lowest-energy Li configuration are given in Table S1 in Supporting Information. In this configuration, the unmodulated phase is favored above the modulated phase. It can be seen that the lowest-energy configuration of $\text{Li}_{0.5}\text{FeBO}_3$ favors a pairwise arrangement in which Li ions reside relatively close to each other ($3.4$ Å) in pairs with the $z$ component of the center-of-mass position of these pairs alternating along the $b$-direction. Intuitively, one would expect the Fe$^{2+}$ ions to be closest to the Li$^+$ ions, thereby minimizing the Coulomb repulsion between the Fe ions and the Li ions. This is indeed the case for the extreme phases, that is, LiFeBO$_3$ containing one Li hole and FeBO$_3$ containing on Li ion. Interestingly, this is not the case for the most stable Li configuration of the half-lithiated phase, as the actual Fe$^{2+}$/Fe$^{3+}$-ion distribution in this phase is $61$ meV/f.u. more stable than the Fe$^{2+}$/Fe$^{3+}$-ion distribution predicted to be the most stable by a model minimizing the Coulombic repulsion created by the Li$^+$ ions at the Fe sites. This suggests that the elastic relaxations of the lattice after adding or removing Li$^+$ ions and the Fe–Fe–ion interactions (electrostatic and magnetic) could play an important role in the stabilization of particular Fe$^{2+}$/Fe$^{3+}$-ion arrangements. The same analysis applied to the second, third, and fourth most stable configuration of the $\text{Li}_{0.5}\text{FeBO}_3$ phase shows that the most favorable Fe$^{2+}$/Fe$^{3+}$-ion distribution is the one predicted by only including the effects of the Coulombic potential created by the Li$^+$ ions at the Fe sites. The more complex Fe$^{2+}$/Fe$^{3+}$-ion ordering in the lowest-energy half-lithiated phase is expected to yield a more complex energy landscape of Li-ion diffusion as compared to the active endmembers, in particular at low C-rates, where the equilibrium structure is expected to form. However, for real materials synthesized at room temperature entropic and kinetic effects result in the actual structure containing several of the lowest-energy configurations. Nevertheless, the transport properties of this phase are expected to be representative for the defect configuration.

All intermediate points in the range $0.0 < x < 0.5$ reside above the convex hull in Figure 2a, suggesting that a two-phase reaction could occur in this region, possibly forming a stable $\text{Li}_{0.5}\text{FeBO}_3$–FeBO$_3$ interface during low-C-rate operation in which each phase has had sufficient time to reach its most stable Li configuration. However, this is not the case for the range $0.5 < x < 1.0$, where the lowest-energy configuration at $x = 0.75$ lies $3.3$ meV/f.u. below a line connecting the lowest-energy configurations of the $\text{Li}_{0.5}\text{FeBO}_3$ phase and the LiFeBO$_3$ phase. This value is well below the typical accuracy of a DFT calculation, and it is therefore not possible to state with absolute certainty that the lowest-energy point at $x = 0.75$ lies below a line connecting the lowest-energy phases at $x = 0.5$ and $x = 1.0$, that is, that the $\text{Li}_{0.75}\text{FeBO}_3$ phase is in fact stable. Additionally, even if the $\text{Li}_{0.75}\text{FeBO}_3$ phase was stable, kinetic effects during electrode operation might prevent this phase from reaching its lowest-energy configuration. This scenario
would correspond to the formation of a stable interface between Li$_{0.5}$FeBO$_3$ and the green atoms residing in green polyhedra are Fe$^{3+}$ on which the electron polarons can hop between (polaronic transport is investigated in Section 3.6). The polaron-hopping paths A$_e$-B$_e$-C$_e$-D$_e$-A$'_e$ and A$_h$-B$_h$-C$_h$-D$_h$-A$'_h$ constitute the paths with the lowest barriers required to move electrons and holes, respectively, in the c-direction, where A$_e$, B$_e$, C$_e$, D$_e$ and A$'_e$ denote Fe$^{3+}$ sites and A$_h$, B$_h$, C$_h$, D$_h$ and A$'_h$ denote Fe$^{2+}$ sites. The positions of the Li ions in this configuration are given in Table S1 in Supporting Information. (d) Unit cell of the half-lithiated phase with the Li-ion configuration of the lowest-energy configuration, but with the Fe$^{2+}$/Fe$^{3+}$-ion distribution predicted by the Coulombic model mentioned in the main text. (Images generated with the VESTA software package.)

3.3. Ionic Transport in Modulated LiFeBO$_3$ and FeBO$_3$.

In order to determine the influence of the stable half-lithiated phase on the transport properties, NEB calculations were first performed on the modulated, lithiated phase, yielding activation barriers for a Li-hole jump in modulated LiFeBO$_3$ and on the fully delithiated phase, yielding activation barriers for Li-ions jumps in FeBO$_3$; the resulting activation barriers are shown in Figure 4. For transport along the a-axis, the motion of Li ions and Li holes occurs by a jump of 2.49 Å, henceforth referred to as A (following the jump notation of Seo et al.$^8$), with an activation barrier of 0.29 and 0.40 eV for the Li ion and hole, respectively, followed by a 4.06 Å jump out of the LiO$_4$ chain, henceforth referred to as C, with an activation barrier of 1.85 eV for the Li ion. The same jump for a Li hole has a barrier of 1.74 eV, however, it is easier for the Li hole at site X in Figure 4b to move in the a-direction by performing D jumps (instead of C jumps) with barrier of only 1.16 eV. The C (D) jump mechanism also constitutes the lowest-energy pathway in which the Li ions (holes) can jump in order to move between the corner-sharing LiO$_4$ chains shown in Figure 4b. For Li transport along the b-axis, Li ions/holes are required to make a 5 Å jump, which would result in a prohibitively high activation barrier, effectively making this transport mechanism inactive. For ionic transport along the c-axis, the Li ions and holes have to overcome two barriers: An A jump (2.49 Å for Li ions and 3.10 Å for Li holes) with an activation barrier of 0.29 eV for the Li ions and 0.40 eV for the Li holes, and a jump of 3.58 Å for Li ions and 3.00 Å for Li holes, henceforth referred to as B (following the jump notation of Seo et al.$^3$), with an activation barrier of 0.75 eV for Li ions and 0.61 eV for the Li holes. It is interesting to note that Li at site X changes position from tetrahedron T$_1$ (see Figure 4b) to T$_2$ (see Figure 4a) upon full delithiation while at the same time increasing the B jump length and decreasing the A jump length. This is also reflected in the activation barriers for Li-ion diffusion as the B barrier is more than twice the magnitude of the A barrier. The paths with their corresponding activation-barrier profiles are shown in Table 1. Additionally, we have calculated activation barriers for Li-hole diffusion in the unmodulated phase shown in Figure S1. However, the barriers do not change significantly compared to the modulated phase of LiFeBO$_3$.

A previous study by Seo et al.$^8$ found lower Li-hole barriers of 0.223 eV for the A jump and 0.437 eV for the B jump that correspond to a Li-hole diffusivity of about $3.7 \times 10^{-10}$ cm$^2$/s (here using a prefactor of $\nu = 10^{-15}$ s$^{-1}$). The apparent
Table 1. Jump Lengths, Activation Barriers, and the Corresponding One-Dimensional Diffusional Constants for Li Transport in the c-Direction†

<table>
<thead>
<tr>
<th>Jump</th>
<th>Activation Barrier, $E_{act}$ [eV]</th>
<th>Diffusivity, $D$ [cm$^2$/s]</th>
<th>Experimental Diffusivity [cm$^2$/s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li ion in FeBO$_3$</td>
<td>A 2.49 0.29</td>
<td>$5.6 \times 10^{-15}$</td>
<td>5.63 $\times 10^{-14}$</td>
</tr>
<tr>
<td></td>
<td>B 3.58 0.75</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>C 4.06 1.85</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Li hole in modulated LiFeBO$_3$</td>
<td>A 3.10 0.40</td>
<td>$1.3 \times 10^{-11}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>B 3.00 0.61</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>C 4.77 1.74</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>D 4.02 1.16</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

†The channular diffusivity is calculated as $D = \bar{P}k$, where $l$ is the jump length and $k$ is the total rate constant that is calculated from $k_{tot} = \sum_{n=1}^{N} k_n^l N$, where $N$ is the number of jumps a Li ion/hole needs to perform in order to move in the c-direction, that is, $N = 2$ (A or B), $k_n^l = \nu e^{-2\sigma_n/k_BT}$ is the rate constant for an elementary jump (that is, A or B), where $\nu = 10^{13}$ s$^{-1}$ is a typical prefactor, $E_{act}$ is the activation barrier for the $n$th elementary jump, $k_B$ is Boltzmann’s constant, and $T$ is the absolute temperature, which is here taken to be room temperature, and $\sigma_n$ is a symmetry factor, which in the present case is unity. Diffusivity is for Li concentration below 0.5 (private communication with Cambaz et al.).

should be noted, that a +U correction will tend to penalize the movement of the diffusing species at the transition state of the migration process and thereby result in a possible overestimation of the activation barrier. Whereas the DFT barriers of Seo et al. might be taken as a lower bound of the true activation barriers, the DFT+U-calculated barriers presented in this study serve as an upper bound on the true activation barriers. However, we point out that our calculated Li-ion diffusion coefficient of $5.6 \times 10^{-15}$ cm$^2$/s agrees well with the experimental value of $5.63 \times 10^{-14}$ cm$^2$/s measured by Cambaz et al. using cyclic voltammetry, motivating our use of the Hubbard-U correction. Despite the aforementioned barrier discrepancy, the ordering of the barriers, that is, $E_{act}^A < E_{act}^B$, is consistent with the results of Seo et al. even with the commensurate modulation included.

The calculations above, summarized in Table 1, show that the transport of Li ions and holes in bulk LiFeBO$_3$ occurs predominantly along the c-axis in nonlinear channels, constituted by corner-sharing LiO$_4$ complexes. Only two distinct types of jumps are needed for macroscopic transport, and the A and B jumps will thus dominate the macroscopic diffusion.

3.4. Ionic Transport in Li$_{0.5}$FeBO$_3$. In order to obtain the kinetic barriers for Li diffusion in the half-lithiated phase, the energy of a Li configuration in which the Li-ion motion is constrained to one channel (extending along the c-axis) relative to the lowest-energy half-lithiated configuration was mapped out in Figure 5 (indicated by the blue line). In these channels, two Li ions, Li$^+$ and Li$^–$, move via the combined A and B jumps shown in Figure 4: The Li$^+$ jump between configuration A and B1 corresponds to an A jump in the endmembers (FeBO$_3$/LiFeBO$_3$), the Li$^+$ jump from configuration B1 to C corresponds to an endmember B jump, the Li$^–$ jump from configuration C to D1 corresponds to an endmember B jump, the Li$^-$ jump from configuration D1 to E corresponds to an endmember A jump, the Li$^–$ jump from configuration E to B2...
not surprisingly, because Li diffusion in the Li-poor region (Li0.5FeBO3), which is about 0.1 eV higher than having the Li hole in the Li-rich region (green point). The barriers during charge (0.32 eV) and discharge (0.19 eV) are both much lower compared to the di FF barrier in FeBO3 (0.75 eV) because the Li distance of 2.98 Å) and thereby increases its Coulombic repulsion. The diffusivity associated with two Li ions jumping from A to A (that is, with a jump length of c = 10.35 Å) is 3.3 × 10−26 cm2/s, which is much lower than the diffusivity associated with Li-transport in FeBO3 (5.6 × 10−12 cm2/s) and Li-hole transport in LiFeBO3 (1.9 × 10−12 cm2/s), indicating that the Li diffusion is strongly impeded in the half-lithiated phase.

3.5. The LiFeBO3-Li0.5FeBO3 Interface. Our convex-hull analysis in Figure 2 and previous GITT experiments2,15,16 suggest that a stable interface between a fully lithiated and half-lithiated phase could be formed. During discharge, Li ions from the Li0.5FeBO3 phase will accumulate at the interface between LiFeBO3 and Li0.5FeBO3 and in order to determine the effects on the Li transport at this interface, the Li diffusion occurring in close vicinity of an interface between LiFeBO3 containing a Li hole and Li0.5FeBO3 was investigated through a NEB calculation. The pathway with the associated activation barrier is shown in Figure 6. Also indicated is the energy level of the interface structure in which the Li hole resides at the interface in the Li-poor region (Li0.5FeBO3), which is about 0.1 eV higher than having the Li hole in the Li-rich region (green point). The barriers during charge (0.32 eV) and discharge (0.19 eV) are both much lower compared to the diffusion barriers of Li ions in FeBO3 and Li holes in LiFeBO3. This is not surprisingly, because Li diffusion across the LiFeBO3−FeBO3 interface, found in Figure S3 in Supporting Information, also displayed lower barriers than those for Li-ion/hole in FeBO3/LiFeBO3. Hence, Li diffusion in the interfacial region between the LiFeBO3 phase containing a Li hole and the Li0.5FeBO3 phase is not expected to be impeded due to the interfaces per se.

3.6. Electronic Transport. During discharge of the Li0.5FeBO3 phase, hole polarons have to traverse a shell of the LiFeBO3 phase in order to recombine with Li ions being inserted into the Li0.5FeBO3 core. In the following, investigations of electron-polaron transport in FeBO3 and hole-polaron transport in LiFeBO3 have been conducted to determine possible polaronic limitations to the charge-discharge process.

We found that upon adding (removing) an electron to FeBO3 (from modulated LiFeBO3), an electron (hole) polaron...
was localized at an Fe\textsuperscript{3+} (Fe\textsuperscript{2+}) ion, increasing (decreasing) the bond lengths by 0.14 Å (0.12 Å) and changing the magnetic moment from 4.29 \(\mu_B\) (3.79 \(\mu_B\)) to 3.79 \(\mu_B\) (4.27 \(\mu_B\)). According to the Mulliken criterion\textsuperscript{32} calculated magnetic moments of 3.75 and 3.79 \(\mu_B\) correspond to a nominal magnetic moment of 4 \(\mu_B\) originating from the unpaired spin counts of the d\textsuperscript{6} ion Fe\textsuperscript{2+}, and 4.29 \(\mu_B\) and 4.27 \(\mu_B\) correspond to a nominal magnetic moment of 5 \(\mu_B\) originating from the unpaired spin counts of the d\textsuperscript{5} ion Fe\textsuperscript{3+}. In the lowest-energy configuration of the half-lithiated phase shown in Figure 3, an electron (hole) polaron was found to be more stable than a delocalized electron (hole) by 0.65 eV (0.47 eV). In Li\textsubscript{0.5}FeBO\textsubscript{3}, the polaron-hosting Fe ion showed the same trends as those in the active endmembers. Upon adding (removing) an electron to FeBO\textsubscript{3} (from modulated LiFeBO\textsubscript{3}), an electron (hole) polaron was localized at a neighboring Fe\textsuperscript{3+} (Fe\textsuperscript{2+}) ion, an increase (decrease) in the Fe–O bond lengths by 0.13 Å (0.12 Å) and a moment change from 4.27 \(\mu_B\) (3.77 \(\mu_B\)) to 3.76 \(\mu_B\) (4.29 \(\mu_B\)), corresponding to nominal magnetic moment 4 \(\mu_B\) (5 \(\mu_B\)) was observed, proving the existence of electron and hole polarons in the half-lithiated phase.

In order to determine possible limitations on the electrochemical performance of Li\textsubscript{x}FeBO\textsubscript{3} originating from effects related to the electronic transport, NEB calculations of polaron jumps in bulk FeBO\textsubscript{3} and LiFeBO\textsubscript{3} were conducted for feasible electron- and hole-polaron hops, shown in Figure 7, namely a polaron hop from Fe site Ap to Fe site Bp (abbreviated Ap-Bp), a polaron hop from Fe site Ap to Fe site Cp (abbreviated Ap-Cp), a polaron hop from Fe site Ap to Fe site Dp (abbreviated Ap-Dp), a polaron hop from Fe site Ap to Fe site Ep (abbreviated Ap-Ep), a polaron hop from Fe site Ap to Fe site Fp (abbreviated Ap-Fp), a polaron hop from Fe site Ap to Fe site Gp (abbreviated Ap-Gp), and a polaron hop from Fe site Ap to Fe site Hp (abbreviated Ap-Hp) with the associated calculated NEB barriers shown in Figure 7b,c. Movement of both electron and hole polarons along the a-axis as well as along the b-axis is possible via two Ap-Dp hops with the barrier being 0.15 eV for the hole polaron and 0.14 eV for the electron polaron. The movement of polarons along the c-axis is achieved by the combined hopping mechanism of Ap-Bp, Ap-Cp, and Ap-Hp with the highest barrier being 0.15 eV (Ap-Hp hop) for the hole polaron and 0.19 eV (Ap-Cp hop) for the electron-polaron. All electron-polaron activation barriers are seen to be well below the delocalization energy of 0.57 eV (vide Figure 7) required to delocalize the electron polaron. It was not possible to find a delocalized solution for hole polarons in the modulated phase.

Figure 7. (a) Polaronic hops from Fe site Ap to neighboring Fe sites Bp, Cp, Dp, Ep, Fp, Gp, and Hp with associated activation barriers for hole-polaron hops in LiFeBO\textsubscript{3} and (b) electron-polaron hops in FeBO\textsubscript{3} (c). *This hole-polaron hop between Ap and Cp is that of the unmodulated phase.
indicating that hole polarons are particularly stable in this phase. Additionally, we have calculated the activation barriers for hole-polaron hopping in unmodulated LiFeBO₃ which are shown in Figure S4 in Supporting Information, and by comparing these results with those for the modulated phase in Figure 7c no significant change in the hole-polaron barriers upon modulation is observed.

Considering the most stable half-lithiated structure in Figure 3 found in the convex-hull analysis of Figure 2 for a hole polaron hopping through this half-lithiated phase, the highest barrier for the lowest-barrier path, AₓBₓCₓDₓA′ₓ₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋ième-Path length, recent studies 34,35 have shown that substitution of Fe by other transition metals could be used to explain whether these Li-electrode materials could still travel through the half-lithiated phase but the barrier could still be stable by Yamada et al. 2 was not found to be stable in our study. Our barriers for Li-ion and hole transport in bulk LiFeBO₃ phases indicated highly anisotropic Li-ion motion with the lowest-barrier pathway being along the c-axis with an associated diffusivity of 5.6 × 10⁻¹⁵ cm²/s for Li-ion diffusion in good agreement with experiments (5.6 × 10⁻¹⁴ cm²/s). It was shown that the Li diffusion in the bulk of Liₓ₂FeBO₃ limited the overall Li diffusion in the active material. Electronic conduction was shown to be mediated by small electron and hole polarons with relatively low hopping barriers in FeBO₃ and LiFeBO₃ but relatively high hopping barriers in Liₓ₀.₅FeBO₃. This barrier increase lowers the mobility of the polarons as they enter the half-lithiated phase. On the contrary, the Li diffusion in the vicinity of an interface between LiₓFeBO₃ containing a hole and Liₓ₀.₅FeBO₃ during charge/discharge is not expected to reduce the overall Li-ion/hole diffusion in LiₓFeBO₃ because the associated kinetic barriers are lower than those associated with Li-ion/hole delithiation in the half-lithiated phases. Interestingly, the barriers for Li-hole diffusion and hole-polaron hopping in the modulated phase were found to the same as those in the unmodulated phase. Hence, in the transport model presented here the combined intrinsic reduction of Li-ion and electron/hole-polaron mobility in bulk LiₓFeBO₃ relative to LiFeBO₃ and FeBO₃ could explain the experimentally reported large overvoltage at initial-stage delithiation of LiFeBO₃. Remedies for these transport-related issues might be found in decreasing the size of the LiFeBO₃ particles and substituting some of the Fe atoms by other cations. 39 Work along this line is now underway.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.6b03456.

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Fractional coordinates of the Li atoms in the most stable configuration of Liₓ₀.₅FeBO₃, NEB-calculated activation barriers for Li-hole diffusion in unmodulated LiFeBO₃, NEB-calculated activation barriers for diffusion of Li ions in half-lithiated phases, results on calculations of transport across the LiFeBO₃–FeBO₃ interface and NEB-calculated activation barriers for hole–polaron hopping in unmodulated LiFeBO₃ (PDF)

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