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1. Introduction

Today’s society is in urgent need of improved media for energy storage that can be used in portable electrics, electric vehicles and large-scale grid-based storage systems of renewable energy. In particular, batteries hold great potential as alternatives to limited and CO₂-emitting fossil fuels for vehicular propulsion.

Despite being a high-capacity cathode material displaying excellent cyclability, LiNi_{1/3}Mn_{1/3}Co_{1/3}O₂ (NMC) is restricted by the toxicity and high cost of Co. Alternative cathode materials include the interesting Li₃VO₂F compound showing excellent rate capability and high specific capacity,¹ though currently limited by high price, and the transition-metal olivine-structured compound, LiFePO₄, attracting interest due to its earth-abundant, environmentally benign elements, but is yet impeded by poor rate capability stemming from a low ionic and electronic conductivity,² which has so far only been improved by decreasing the LiFePO₄ particle size, and decreasing the volumetric energy density.

In recent years, lithium iron borate (LiFeBO₃) has received increasing interest due to its low-cost constituents, a relatively high specific capacity of 220 mA h g⁻¹ and the very small volume change during operation of about 2%,³ which lowers the risk of losing contact with the other battery components. However, pristine LiFeBO₃ compounds are prone to oxidation from ambient air and moisture, and studies by Yamada et al.⁴,⁵ have clarified the detrimental effects of air oxidation on LiFeBO₃ electrodes, which were shown to involve the displacement of Fe onto the Li sites as Li was leached out of the active LiFeBO₃ material.⁴ Coating the LiFeBO₃ electrode with a carbonaceous species has therefore become instrumental in protecting the electrode from oxidation and thereby improving the electro-chemical performance of the material.

There exist numerous experimental studies which report on the beneficial properties endowed by carbon-coating the electrode material. Both hexagonal and monoclinic LiMnBO₃ have been shown to benefit from being carbon-coated, showing a reduction in polarization and a correspondingly large increase in the reversible capacity from 65 mA h g⁻¹ to 100 mA h g⁻¹.

A density functional theory study of the carbon-coating effects on lithium iron borate battery electrodes†

Simon Loftager, Juan María García-Lastra and Tejs Vegge*

Lithium iron borate (LiFeBO₃) is a promising cathode material due to its high theoretical specific capacity, inexpensive components and small volume change during operation. Yet, challenges related to severe air- and moisture-induced degradation have prompted the utilization of a protective coating on the electrode which also improves the electronic conductivity. However, not much is known about the preferential geometries of the coating as well as how these coating–electrode interfaces influence the lithium diffusion between the coating and the electrode. Here, we therefore present a density functional theory (DFT) study of the anchoring configurations of carbon coating on the LiFeBO₃ electrode and its implications on the interfacial lithium diffusion. Due to large barriers associated with Li-ion diffusion through a parallel-oriented pristine graphene coating on the FeBO₃ and LiFeBO₃ electrode surfaces, large structural defects in the graphene coating are required for fast Li-ion diffusion. However, such defects are expected to exist only in small concentrations due to their high formation energies. Alternative coating geometries were therefore investigated, and the configuration in which the coating layers were anchored normal to the electrode surface at B and O atoms was found to be most stable. Nudged elastic band (NEB) calculations of the lithium diffusion barriers across the interface between the optimally oriented coating layers and the electrode show no kinetic limitations for lithium extraction and insertion. Additionally, this graphite-coating configuration showed partial blocking of electrode-degrading species.
at C/20.\(^6\) LiFePO\(_4\) has also been shown to have its rate capability and reversible capacity greatly improved by carbon-coating the electrode,\(^7\)\(^9\) and a study by Zhou et al.\(^{10}\) in which LiFePO\(_4\) electrode particles were homogeneously and loosely wrapped with a graphene three-dimensional network suggested that this was attributed to smaller particle sizes, improved electronic conductivity due to higher graphitization and to an extended three-dimensional network graphene wrapping in which the voids between the graphene layers and the electrode easily enabled the diffusion of Li ions between the LiFePO\(_4\) crystal and the electrolyte.

In this computational study, the protective coating on the active LiFePO\(_4\) electrode surface is modeled as carbon-coating layers on the LiFePO\(_4\) electrode surface. The optimal anchoring was found to be that in which the coating-edge C atoms bond to electrode-surface B and O atoms and the coating layers are normal to the electrode surface. The analysis is combined with an assessment of the rate of lithium transport through different possible configurations of the carbon coatings, indicating no kinetic limitations to Li (de)insertion of the electrode across the kinetic limitations to Li (de)insertion of the electrode across the voids between the graphene layers and the electrode easily enabled the diffusion of Li ions between the LiFePO\(_4\) crystal and the electrolyte.

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2. Computational details

2.1. The crystal structure of LiFeBO\(_3\)

LiFeBO\(_3\) has a monoclinic crystal system in which FeO\(_5\) complexes link together at the edges forming chains along the [101] direction, and chains of LiO\(_2\) complexes run along the [001] direction. Boron and oxygen atoms form trigonal groups which connect the edge-sharing FeO\(_5\) chains. The crystal structure of LiFeBO\(_3\) is shown in Fig. 1. A commensurate modulation of the LiFeBO\(_3\) structure was optimized starting from the experimental lattice constants reported by Janssen et al.\(^{11}\) \(a = 5.1350\) Å, \(b = 9.0437\) Å, \(c = 10.2907\) Å and \(\beta = 91.031^\circ\). As Li ions are extracted from LiFeBO\(_3\) during charge, the Fe\(^{2+}\) ions are oxidized to Fe\(^{3+}\). The Fe ions were consistently found to be in their high-spin state having their five 3d orbitals occupied. Hence, Fe in LiFeBO\(_3\) is Fe\(^{3+}\) having a magnetic moment of 4 \(\mu_B\) and Fe in FeBO\(_3\) is Fe\(^{3+}\) having a magnetic moment of 5 \(\mu_B\).

2.2. Computational methods

In this study, input structures were built and analyzed using the Atomic Simulation Environment (ASE) package\(^{14}\) and structurally relaxed to their equilibrium structure by solving the electronic-structure problem within DFT. The DFT implementation in Vienna Ab initio Simulation Package (VASP)\(^{15}\) was used with plane waves being expanded up to a kinetic-energy cutoff of 500 eV. The projector-augmented-wave (PAW) method\(^{16}\) was used to model the atomic cores, and in the PAW potentials, for Li, B and O the 1s electrons were treated as core electrons, and for Fe the 1s, 2s, 2p, 3s and 3p electron shells were treated as core electrons. The exchange and correlation effects were modeled within the generalized-gradient approximation (GGA) by the Perdew–Burke–Ernzerhof (PBE) parametrization.\(^{17}\) The partial occupations were determined using the tetrahedron method with Blochl corrections, and the electronic levels were smeared by 0.05 eV.

Due to the incomplete cancellation of the electron self-interaction (SI) error inherent in the GGA, calculated properties, such as the band gap, can deviate significantly from experimental values,\(^{18,19}\) stemming from the SI-induced delocalization of the electrons within this model, especially for systems having strongly localized d-orbital electrons, such as LiFeBO\(_3\). Previous studies have efficiently rectified the SI error in the GGA by employing the Hubbard-U correction scheme\(^{20}\) and following the work by Seo et al.\(^{21}\) a Hubbard U of 4.3 eV in the rotationally invariant scheme from the study of Dudarev et al.\(^{22}\) was applied on the 3d orbitals of Fe in FeBO\(_3\) and LiFeBO\(_3\). To correctly model the van der Waals (vdW) interaction between the graphene layers, a vdW-based functional should in principle be employed. Only a few previous studies\(^9,23\) have combined Hubbard corrections with a vdW functional, however, it is not yet a well-established, widely used approach to employ such vdW+U functionals. Generally, the error introduced by having a slightly incorrect coating-layer separation is not expected to be significant. For instance, by stretching graphite along the layer stacking (c) direction and changing the experimental observed layer separation from 3.39 Å to 4.94 Å (corresponding to half of the b lattice parameter for FeBO\(_3\) used later in this study as the coating-layer separation), the energy of the system per C atom only changed by 9.6 meV. Likewise, the interaction between the parallel graphene coating and the FeBO\(_3\)/LiFeBO\(_3\) electrodes (see Fig. 2) is expected to be small, as the coating-electrode separation is large: a fit to the shifted total energies in Fig. S1(a) (ESI) calculated using the BEEF-vdW functional\(^{24}\) with the Hubbard-U correction

![Fig. 1 Unit cell of LiFeBO3 with Fe atoms in the center of the brown edge-sharing FeO5 complexes forming chains along the [101] direction and Li atoms in purple LiO2 complexes forming chains in the [001] direction. Images were generated using the VESTA software package.\(^{13}\)](image-url)
LiFeBO3 separation is 3.7 Å. This is only slightly smaller than that predicted by the PBE+U functional when the coating-electrode interactions become negligible at about 4.0 Å as seen in Fig. S1(b) (ESI†). As previously stated the combination of a vdW functional and Hubbard corrections has not been thoroughly tested yet, and we have therefore adhered to the widely deployed PBE+U functional.

The unit cell and internal coordinates of FeBO3 and LiFeBO3 were fully relaxed to their equilibrium geometry such that the forces on the atoms did not exceed 0.05 eV Å⁻¹ using the Fast Inertial Relaxation Engine (FIRE) minimization algorithm25 and the Brillouin zone was sampled using a Monkhorst-Pack (MP) mesh of $4 \times 2 \times 2$. The simulation cell used in the subsequent relaxation of the coating-electrode structures was inherited from the unit-cell dimensions of FeBO3 and LiFeBO3 for Li-ion and Li-vacancy calculations, respectively, with vacuum added in the c-direction so as to form a (001) surface of the FeBO3/LiFeBO3 electrodes and the two bottommost electrode layers were kept spatially fixed. For such supercells, an MP mesh of $4 \times 2 \times 1$ was used. In calculations simulating Li insertion or Li-vacancy formation, the aforementioned supercells were doubled in the c-direction and a $2 \times 2 \times 1$ MP mesh was used. The two bottom layers of the coated electrodes were fixed. For all structure relaxations, the self-consistent solution to the Kohn–Sham equation was performed with an accuracy of 0.1 meV.

For the determination of the activation barriers of the Li-ion diffusion across the coating-electrode interface, the nudged elastic band (NEB) method26 implemented in ASE was utilized for Li-ion pathway interpolating between the initial and final images. The energies were calculated using VASP, and the structure relaxations (0.05 eV Å⁻¹) were let to relax to the same threshold value as for the structure relaxations (0.05 eV Å⁻¹) using the FIRE algorithm.

3. Results and discussion

3.1. DFT-optimized lattice of bulk LiFeBO3 and FeBO3

Upon relaxation of all internal degrees of freedom, the lattice parameters for the LiFeBO3 unit cell were found to be $a = 5.168$ Å, $b = 9.109$ Å, $c = 10.349$ Å and $\beta = 91.28^\circ$ in good agreement with experimental values11 (see above). The lattice parameters of the FeBO3 unit cell were found to be $a = 5.308$ Å, $b = 8.989$ Å, $c = 10.188$ Å and $\beta = 89.40^\circ$ giving rise to a volume contraction upon fully delithiating LiFeBO3 to FeBO3 of 0.2%.

3.2. Parallel-oriented coating on FeBO3/LiFeBO3 electrodes

Graphene sheets oriented parallel to metal surfaces have previously been found to bind via chemisorption or physisorption depending on the substrate,9,27 and we have therefore investigated the effects of arranging the graphene sheet parallel to the surfaces of the FeBO3 and LiFeBO3 electrodes.

In order to determine the most stable low-index surface of the LiFeBO3 electrode, the surface energies, listed in Table 1, were calculated for the lowest-index surfaces, i.e. the (100), (010) and (001) LiFeBO3 surfaces. It is seen that the (001) surface is approximately three times more stable (15 meV Å⁻²) as the other two surfaces (41 and 47 meV Å⁻²). The surfaces are shown in Fig. S2 (ESI†). It is therefore expected that the (001) surface will be the most dominant surface involved in the formation of external interfaces.

The surfaces of some oxide materials,28,29 such as LiNi0.5Mn1.5O4, Co1-xO2 and Li1xMnO2, are known to display reconstruction. However, in this study no indications of such surface reconstruction were observed for the FeBO3 or LiFeBO3 electrodes. Yet, it should be noted that surface reconstruction often exists over large areas which could not be captured by our relatively small simulation cells.

The (001) surface of the FeBO3 electrode can be covered by a pure graphene sheet with an expansive strain on graphene of only 7.5% along the a-axis and 5.1% along the b-axis with a resulting strain energy of 239 meV per C atom, and the (001) surface of the LiFeBO3 electrode can be covered by a pure graphene sheet with an expansive strain of only 4.7% along the a-axis and 6.5% along the b-axis with a resulting strain energy of 192 meV per C. However, due to the large separation between the parallel-oriented graphene coating and the FeBO3/LiFeBO3 surfaces of 4.0 Å (3.7 Å if vdW effects are taken into account; see S1 in the ESI†), as seen in Fig. 2, the interaction between the coating and the electrodes is found to be very small. Therefore, the two subsystems will be treated separately for the case of having the graphene coating parallel to the (001) electrode surface.

The surface lithiation/delithiation processes can therefore to a first approximation be analyzed by studying the surface electrodes shown in Fig. 3.

As listed in Table 2, for the bulk electrode the insertion energy is 3.26 eV and the vacancy-formation energy is 2.90 eV versus Li(s) with the bulk equilibrium voltage being 3.08 V.

### Table 1. Surface energies for low-index surfaces of the LiFeBO3 electrode

<table>
<thead>
<tr>
<th>Surface</th>
<th>Surface energy [meV Å⁻²]</th>
</tr>
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<tr>
<td>(100)</td>
<td>41</td>
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<tr>
<td>(010)</td>
<td>47</td>
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<td>(001)</td>
<td>15</td>
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versus Li(s). The presence of the (001) surfaces shown in Fig. 3 makes it more favorable for the Li ions to be inserted in the outermost layer of the electrode as the insertion energy is 3.47 eV and the vacancy-formation energy is 3.22 eV, i.e. higher than those for the bulk electrode. In a calculation, a Li ion initially 3 Å above the LiFeBO3 electrode surface was seen to absorb into the surface layer of the electrode with no kinetic barriers to overcome. The energy gain (3.47 eV) of this process is much larger than the Li adsorption energy on pristine graphene, 1.7 eV as shown in Fig. S3 (ESI†), suggesting that a Li ion adsorbed on the graphene coating on the electrode side would presumably have a negligible kinetic barrier toward insertion of the Li ion into the electrode surface layer. On the other hand, it is well known that the diffusion barrier of the Li ion through pristine graphene is very high,30 warranting further investigations into the effect of the graphene defects on the Li diffusion through the coating.

Li transport through the hollow site of pristine graphene, through graphene with a monovacancy and through graphene with a 5-8-5 divacancy was investigated using the NEB method which yielded the results shown in Fig. S4 (ESI†). As listed in Table 3, the barrier for Li-ion diffusion through a hollow site of pristine graphene is 7.41 eV, agreeing well with a previous study.31 The barrier for Li diffusion through a graphene monovacancy is 7.84 eV, and through a 5-8-5 divacancy 1.11 eV. In a calculation, FeBO3/LiFeBO3 particles and 1–3 monolayers of carbon coating (Fig. 4(d) in the study of Zhang et al.) and similar observations were reported by Tao et al.16 on carbon-coated LiFeBO3 nanoparticles (Fig. 9(b) in the study of Tao et al.). We have therefore investigated the effects of an angular misalignment of the carbon-coating layers on the FeBO3 and LiFeBO3 electrodes. The coating is here modeled as graphite layers whose edges opposite to the electrode are terminated by hydrogen atoms to avoid dangling bonds. Various positions on the electrode surface at which the coating could anchor were investigated using one graphite layer per unit cell, placed normal to the electrode surface. The graphene coating was strained expansively to the electrode unit cell and the strain of the graphite layer in the electrode a-direction was 7.5% for the FeBO3 electrode yielding a strain energy (i.e. the energy difference between unstrained and strained graphene coating) of 141 meV per C and 4.7% for the LiFeBO3 electrode with a strain energy of 62 meV per C. For both electrodes, the most stable anchoring configuration was found to be that in which one of the coating-edge C atoms bonded to a B atom with a bond length of 1.63 Å and 1.60 Å for FeBO3 and LiFeBO3, respectively, and the other coating-edge C atom bonded to an O atom with a bond length of 1.27 Å and 1.36 Å for FeBO3 and LiFeBO3, respectively, as shown in Fig. 4, indicating that the graphite coating is chemisorbed on the electrode surface. This anchoring arrangement was found to be 284 meV and 470 meV per surface-bonding C atom (four per unit cell) more stable than the second-lowest-energy anchoring configuration in which the C atom which previously bonded to the B atom now bonded to an Fe atom in FeBO3 and LiFeBO3, respectively, shown in Fig. S5 (ESI†).
The relative stability of the coating–electrode interface versus the angle between the carbon coating and the electrode is shown in Fig. 5. From here the optimal angular configuration between the electrode (001) surface and the coating plane hinged to the aforementioned B atom and the O atom was found to be that in which the graphene coating was positioned normal to the electrode surface (vide Fig. 4). The distance between the coating layers in the b-direction was 4.49 Å for FeBO$_3$ and 4.55 Å for LiFeBO$_3$. In this optimal configuration the graphite layers are stacked as AA along the b-axis. Calculations on a structure possessing only one coating layer per unit cell—resulting in a layer spacing of the b lattice parameter—showed identical results, implying that having a less dense distribution of coating layers on the FeBO$_3$/LiFeBO$_3$ surface does not alter the predictions of the angular coating orientation made by the aforementioned study with two graphite layers per unit cell.

Using the optimal coating–electrode geometry shown in Fig. 4, the potential of a Li ion in a graphitic anode, in the graphite coating attached to the electrode, in the coated electrode surface layer and in bulk FeBO$_3$ during initial-stage discharge was calculated and is depicted in Fig. 6(a). A potential drop of 2.22 V during Li-ion diffusion from the hollow site of graphite closest to the electrode surface into the surface layer of the electrode was found. Interestingly, a Li ion stabilizes in the surface layer of FeBO$_3$ compared to being inserted into bulk FeBO$_3$ by 0.17 eV. However, as more Li ions are inserted from the graphite coating, the Li ion in the electrode surface layer is pushed further into the interior of the positive electrode due to the Li–Li repulsion. Additionally, the electric-potential landscape for a Li ion during final-stage discharge is mapped out in Fig. 6(b). Here, it is noteworthy that the potential of the Li ion inserted into the electrode surface layer (versus metallic Li) is 1.12 V smaller than the potential of a Li ion inserted into the vacancy-containing bulk electrode. This implies that a significant part of the experimentally observed sloping of the voltage profile near the end of discharge in LiFeBO$_3$ could come from the difference between the surface and bulk potentials.

In order to determine possible interface-induced kinetic limitations for Li-ion transport between the graphite coating and the electrodes, NEB calculations were carried out at both initial-stage and final-stage discharge. The NEB results in Fig. 8...
show that there are no activation barriers for Li-ion transport across the coating–electrode interface during (a) initial-stage and (b) final-stage discharge (a barrier of 27 meV predicted to exist at the final-stage discharge is easily overcome by thermal excitation of the Li ions at room temperature). In both the charged and discharged configurations, local minima were identified for the Li ion in the graphene coating as shown in the insets in Fig. 7. Hence, the angular configuration of the graphite coating shown in Fig. 4 is found to provide an energetically preferred state with significantly reduced kinetic barriers for lithium to the positive electrode, compared to the parallel graphene coatings (vide Fig. 2).

In a realistic situation the size of the graphene sheets is sufficiently large to expect that the interlayer distance between graphene sheets when they are far from the FeBO$_3$/LiFBO$_3$ electrode will correspond to that of graphite (i.e. 3.39 Å). Looking at Fig. 5, in order to reach this situation we can hypothesize two scenarios: (i) the graphene sheets are anchored perpendicularly to the FeBO$_3$/LiFBO$_3$ electrode, having the graphene interlayer distance of 4.49 Å at the anchoring position. Then the sheets gradually bend until they end up being a distance of 3.39 Å apart. (ii) The graphene sheets are tilted ~48° at the anchoring position, having their interlayer distance 3.39 Å from the starting point. It is difficult to assess which of the two situations will occur in reality since in the latter scenario it is necessary to provide ~0.25 eV per C atom to tilt the graphene sheets 48° while in the former situation it is necessary to spend some energy to bend the graphene. Analyzing the energy associated with the bending of the graphene sheets is not a trivial task as it has been reported in a recent study by Nilsson et al., which combines DFT with experiments, showing that the bending of graphene sheets on top of metallic substrates is strongly dependent on which atoms saturate the edges of the graphene sheets. In any case, even in the scenario of an angling of the whole coating layers around the anchoring sites on the electrode surfaces (as in Fig. 5(b)), the facile Li diffusion across the coating–electrode interface in Fig. 7 is not expected to be impeded due to the relatively open Li pathway across the interface, which persists even for significant angling, such as 47.7° in Fig. 5(b). In this tilted geometry, the Li-ion diffusion far away from the electrode would resemble that of diffusion in graphite, where a relatively low activation barrier for a Li ion jumping between hollow sites of 0.47 eV was found, agreeing well with previous findings. Despite the successful application of carbon-coating the LiFeBO$_3$ electrodes, these materials are still observed to undergo degradation to some extent. In general, the degradation and oxidation of electrode compounds through moisture and air attack under ambient conditions are well-established in the literature and in this study these degradative species were modeled as H$_2$O and O$_2$. Interestingly, we found that the activation barrier for O$_2$ diffusion in graphite (i.e. the coating far from the electrode surface) at very low concentrations is higher than that for Li diffusion in the same graphite coating, that is, 1.0 eV for O$_2$ diffusion as shown in Fig. S6 (ESI†). In contrast, water was found to diffuse quite easily in graphite with a barrier of only 0.1 eV for jumps between the hollow sites, agreeing well with a relatively low binding energy of water on graphene sheets. This indicates that the graphite coating...
coating could act as a filter allowing Li ions to diffuse relatively easily across the carbon coating down into the electrode surface during discharge while preventing the degradative O₂ species from reaching the electrode surface, however, without being able to block all degradative species, such as H₂O, which could explain that degradation occurs even in carbon-coated electrode materials.

For the perpendicular-coating-LiFeBO₃ interfaces shown in Fig. 4, it is found that a Li ion positioned at the upper hollow site not terminated by hydrogen atoms has approximately the same energy as when positioned in the lowest hollow site (just above the electrode as shown in the insets of Fig. 7), both being favored by approximately 1 eV compared to the negative-electrode side. NEB results—shown in Fig. 8—yield an activation barrier of 0.2 eV for Li-ion diffusion between the two hollow sites in the LiFeBO₃ electrode.

4. Conclusions

Using DFT, stability investigations into different graphene-coating structures and the angular orientation of the graphene coating were carried out, as well as the role of defects in the carbon coating in the lithium transport mechanisms. Based on the calculations, it was found that large structural defects and/or significant misalignments between the carbon coatings and the FeBO₃/LiFeBO₃ nanoparticles provide mechanisms for facile Li-ion diffusion during charge and discharge. However, significant formation energies of the defects commonly observed in graphene imply low equilibrium concentrations of these defects. Alternative coating geometries where the coating layers were allowed to chemisorb on the surface, the diffusion of the electrode-degrading species, O₂, was seen to be very low due to a high activation barrier, whereas another electrode-degrading species, H₂O, was seen to easily diffuse in the graphite due to a low barrier of 0.1 eV, indicating that the perpendicularly anchored coatingconfiguration partially protects the electrode from degradation under ambient conditions. Furthermore, the Li-ion diffusion in the graphite coating near the electrode was found to be relatively fast due to a low activation barrier of 0.2 eV. These findings tally well with experimental observations which show no indications of limitations in the Li diffusion induced by the application of carbon coating, and instead the overall electrochemical performance is observed to improve.

Acknowledgements

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